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TURBINE ENGINE EXHAUST HYDROCARBON ANALYSIS TASK 1 AND 2

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The environmental impact of organic compounds emitted from jet aircraft turbine engines has not been firmly established, due to the lack of data regarding the emission rates and identities of the compounds. The objective was to identify and quantify the organic compounds present in gaseous emissions from jet engines and to study the photochemical behavior of these compounds. This interim report describes the experimental work performed for Task 1 (sampling and analysis method validation) and Task 2 (combustor rig testing), wherein a variety of sensitive and reliable methods were developed and evaluated		

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for the determination of the wide range of compounds likely to be emitted from jet engines. Tasks 3-5 will be performed between April and September, 1983. At that time emissions from full-scale jet engines will be characterized in terms of chemical composition and photochemical reactivity using a variety of fuels and operating conditions.

Methods developed during Task 1 include a cryogenic trapping technique for C₂-C₁₂ hydrocarbons, a resin adsorption technique for C₈-C₁₈ hydrocarbons, a gas chromatography/mass spectrometry procedure for polynuclear aromatic hydrocarbons (PAH), a HPLC method for aldehydes, and a direct injection gas chromatography photo-ionization (GC/PID) method for alcohols. Recoveries were approximately 90 percent for cryogenic trapping, 85-90 percent for resin adsorption, and 60-100 percent for aldehydes. Precision ranged from approximately ± 5 percent for cryogenic trapping to ± 25 percent for selected aldehydes.

The Task 2 combustor rig test data were very encouraging in that:

(1) 88 percent carbon balance was obtained by comparing the total hydrocarbon concentration to the summation of individual hydrocarbon species, (2) a major portion (~60 percent) of the total hydrocarbon content was attributable to specific compounds determined by GC/MS and (3) good method performance in terms of precision and accuracy (comparable to or better than Task 1 in all cases) was obtained.

PREFACE

This report was prepared by Battelle, Columbus Laboratories, Columbus, Ohio 43201, under contract Number F08635-82-C-0131 for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RDV), Tyndall Air Force Base, Florida 32403.

This interim report describes the experimental design of the program and the results obtained for Task 1 (method development) and Task 2 (combustor rig testing). This work was performed between January and September 1982. AFESC (RDVS) project officers were Captains Randy L. Gross and Richard E. Padgett.

Principal research staff at Battelle included Mr. M. W. Holdren, Dr. R. M. Riggin, and Dr. C. W. Spicer. Assistance in conducting the program was provided by Mr. W. E. Bressler, Mr. T. F. Cole, Ms. D. L. Good, Mr. T. L. Hayes, Mr. J. R. Koetz, Ms. M. J. Pepper, Mr. R. N. Smith, and Mr. G. F. Ward. The combustor rig testing portion of the program was conducted under the direction of Mr. T. F. Lyon, General Electric, Cincinnati, Ohio. Technical assistance at the General Electric Combustor Laboratory was provided by Mr. Doug Enochs. Battelle Program Manager was Mr. D. A. Berry.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public including foreign nationals.

This report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION.	1
II	TASK 1. VALIDATION STUDIES	3
	A. CHAMBER VERSUS MANIFOLD SAMPLING.	6
	B. RECOVERY EFFICIENCIES FOR THE ENGINE SIMULATION EXPERIMENTS.	6
	C. PRECISION CHECK	12
	D. CARBON BALANCE.	16
III	TASK 2. COMBUSTOR RIG STUDIES.	20
	A. EXPERIMENTAL.	20
	1. Combustor Test Facility	20
	2. Mobile Laboratory	24
	3. Exhaust Sampling.	24
	4. Biological Assay Sampling	33
	5. Fuel Sampling	34
	B. RESULTS	34
	C. DISCUSSION.	59
	1. Overview.	59
	2. Distribution of Organic Components in Combustor Rig Exhaust	59
	3. Carbon Balance.	68
	4. Method Performance Characteristics.	69
	D. CONCLUSIONS	73
	REFERENCES.	74

LIST OF FIGURES

Figure	Title	Page
1	Sampling System for Task 1 Validation Experiments. .	4
2	Chromatograms Obtained by Cryogenic Techniques (Capillary Column) Demonstrating the Transfer Efficiency of the Sampling System.	8
3	Chromatograms Obtained by XAD Techniques Demon- strating the Transfer Efficiency of the Sampling System	9
4	Chromatograms Obtained by DNPH Aldehyde Techniques Demonstrating the Transfer Efficiency of the Sampling System.	10
5	One-Sixth Sector Combustor From TF-39 Turbine Engine	22
6	Continuous Emissions Analyzers Associated With Combustor Rig Facility	23
7	Mobile Laboratory Located Adjacent to Combustor Rig Facility	25
8	Schematic of Combustor Rig and Sampling System . . .	26
9	GC/FID Chromatogram of JP-5 Fuel Sample From Test 8	37
10	GC/FID Chromatogram of Combustor Rig Exhaust (Test 14) Using On-Line Cryogenic GC	39
11	GC/FID Chromatogram of XAD Exhaust Sample from Test 8	40
12	Chromatogram for DNPH/HPLC Analysis Test 14.	41
13	Chromatogram of Bag Sample Collected During Test 11.	51
14	Chromatogram of Bag Sample Collected During Test 11 After Spiking With 10 ppm Ethanol.	51
15	Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 2, 3 and 4.	54

LIST OF FIGURES
(CONCLUDED)

Figure	Title	Page
16	Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 6, 7 and 8. . .	55
17	Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 10, 11 and 12 .	56
18	Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 14, 15 and 16 .	57

LIST OF TABLES

Table	Title	Page
1	TEST COMPOUNDS FOR METHOD VALIDATION.	5
2	CONDITIONS OF VALIDATION EXPERIMENTS.	6
3	DATA DEMONSTRATING SAMPLING SYSTEM TRANSFER EFFICIENCY.	7
4	RECOVERY EFFICIENCIES FOR ENGINE SIMULATION EXPERIMENTS, BY PERCENT	11
5	COMPARISON OF COMPOUNDS THAT OVERLAP THE ANALYTICAL METHODS	13
6	RECOVERY DATA FOR PAHs SPIKED ON XAD TRAPS PRIOR TO SAMPLING	14
7	PRECISION DATA FOR ENTIRE SAMPLING AND ANALYSIS SYSTEM.	15
8	EXAMPLE CARBON BALANCE CALCULATION (ASSUMES RESPONSE FACTOR OF 1.0 FOR ALL CARBONS)	18
9	CARBON BALANCES FOR SIX VALIDATION EXPERIMENTS. . .	19
10	SAMPLING TECHNIQUES AND PARAMETERS DURING COMBUSTOR RIG TESTS	28
11	ENGINE OPERATING CONDITIONS AND STANDARD EMISSIONS DATA FOR COMBUSTOR RIG TESTS.	36
12	PERCENT COMPOSITION IN JP-5 FUEL FROM COMBUSTOR RIG TESTS	38
13	MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING TECHNIQUE, COMBUSTOR RIG TESTS, 6/23/82	42
14	MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING TECHNIQUE, COMBUSTOR RIG TESTS, 6/24/82	43
15	MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING TECHNIQUE, COMBUSTOR RIG TESTS, 6/30/82	44
16	MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING TECHNIQUE, COMBUSTOR RIG TESTS, 7/1/82	45

LIST OF TABLES
(CONCLUDED)

Table	Title	Page
17	MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING TECHNIQUE, COMBUSTION RIG TESTS, 6/23/82.	46
18	MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING TECHNIQUE, COMBUSTION RIG TESTS, 6/24/82.	47
19	MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING TECHNIQUE, COMBUSTION RIG TESTS, 6/30/82.	48
20	MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING TECHNIQUE, COMBUSTION RIG TESTS, 7/1/82	49
21	ALDEHYDES QUANTIFIED BY THE DNPH/HPLC TECHNIQUE . .	50
22	PNA CONCENTRATIONS IN SELECTED XAD AND FUEL SAMPLES, $\mu\text{g}/\text{m}^3$	52
23	STANDARD FUELS ANALYSIS DATA.	58
24	SUMMARY OF ORGANIC SPECIES MEASURED BY VARIOUS SAMPLING AND ANALYSIS METHODS, ppmC	60
25	TOTAL ORGANIC SPECIES CONTRIBUTION BY CARBON NUMBER.	61
26	MAJOR IDENTIFIED COMPOUNDS FROM TEST #14 GROUPED INTO THE FOLLOWING CLASSES.	62
27	GC/MS IDENTIFICATION OF EXHAUST AND FUEL COMPONENTS.	64
28	SELECTED AROMATIC/ALIPHATIC HYDROCARBON RATIOS FOR EXHAUST AND JP-5 FUEL	67
29	COMPARISON OF ORGANIC SPECIES SUM WITH TOTAL FID RESPONSE FOR COMBUSTOR RIG EXHAUST.	70

SECTION I

INTRODUCTION

The environmental significance of organic emissions from aircraft turbine engines has not been established, in spite of the completion of numerous studies in the area. Specifically, the contribution of aircraft exhaust organic emissions to photochemical pollutant formation is poorly understood since complete data concerning the qualitative and quantitative chemical composition of these emissions are not available.

Several studies have been conducted to determine the organic chemical composition of jet turbine engines. One study employed subtractive gas chromatography to determine compound classes and selected individual paraffins in jet aircraft emissions under various operating conditions (1). Other studies determined total aldehyde and hydrocarbon emissions under a variety of conditions (2,3). Another study employed a liquid chromatographic technique to separately determine unreactive and reactive hydrocarbons (4). Unfortunately, none of the above studies determined individual organic compounds.

Two studies have been reported in which a large number of individual organic compounds were determined in gas turbine exhaust (5,6). One study (5) qualitatively determined 273 individual organic compounds, but did not attempt to quantify these materials. A second study attempted to perform a quantitative mass balance of the hydrocarbon emissions (6). While relatively good mass balance (85 percent) was obtained by comparing individual species and total hydrocarbons at high thrust, poor mass balance (~32 percent) was obtained under idle operating conditions. Another study demonstrated that particle-bound organic emissions are a very small fraction of the total organic composition of the exhaust and, from a mass balance standpoint, can be ignored (7).

In view of the sparse data available concerning individual organic components in jet turbine exhausts, any estimate of the environmental significance, including photochemical pollutant formation of these emissions, is likely to be highly inaccurate. Consequently, the Environics Division, Air Force Engineering and Services Laboratory, Air Force

Engineering and Services Center, Tyndall AFB, Florida, has contracted with Battelle, Columbus Laboratories (BCL) to perform a comprehensive study of organic emissions from jet aircraft turbine engines.

The specific objectives of this study are as follows:

1. to obtain a detailed analysis of the composition of the gaseous hydrocarbon species emitted in gas turbine engine exhausts.
2. to determine the effect of these hydrocarbons on atmospheric photochemical processes, using an outdoor smog chamber.

This program is to be completed in five separate tasks as follows:

- Task 1 - Development and validation of sampling and analysis procedures for selected organic compounds representative of gas turbine engine emissions.
- Task 2 - Evaluation of the procedures developed in Task 1, using a laboratory combustor rig.
- Task 3 - Identification and quantification of individual organic compounds emitted from two commercial jet engines operated at various thrust settings and burning three different fuels.
- Task 4 - Concurrently, with Task 3, investigate the photochemical behavior of the emissions (at the idle thrust setting), using a Teflon[®] smog chamber.
- Task 5 - Evaluate the data from Tasks 3 and 4 in terms of environmental impact of jet aircraft operations.

This report describes the efforts to date on the above contract. Specifically, the results of Tasks 1 and 2 are presented in subsequent sections of the report.

SECTION II

TASK 1. VALIDATION STUDIES

During Task 1, individual components of the sampling and analysis system were developed and validated for use in combustor rig and engine testing. As specified in the Work Plan, the final test of these components requires a comprehensive validation experiment in which all sampling and analysis systems are operational. The results of several such experiments are described in this section. One set of experiments simulates jet engine idle conditions, and one set simulates high thrust. The sampling system is shown schematically in Figure 1. The heated stainless steel probe, heated pump, heat-traced sampling line and manifold were employed to sample complex organic mixtures from a large environmental chamber. The organic mixture is designed to represent the major constituents of turbine engine exhaust. This mixture is shown in Table 1. To this mixture are added other exhaust constituents such as CO, CO₂, H₂O, and NO_x. The sample probe was heated either to 800°F or 1000°F during the experiments to mimic the surface, residence time, and temperatures the sample gas may experience during actual engine experiments.

The initial conditions of the comprehensive validation experiments are shown in Table 2. Earlier experiments with individual compounds have demonstrated that the sample probe and associated pump, tubing and manifold do not affect the distribution or concentrations of organics being sampled.¹ The remainder of this section of the report describes the results of the comprehensive validation experiments. Detailed descriptions of the various analytical methods are provided in Section III, Part A.

¹ Trimethylpyridine appears to be rapidly lost in the chamber through an unidentified mechanism; hence, prohibiting validation of the sampling and analysis system with this compound. Trimethylpyridine was included in the surrogate exhaust to represent organic nitrogen components likely to be present in shale-derived fuel.

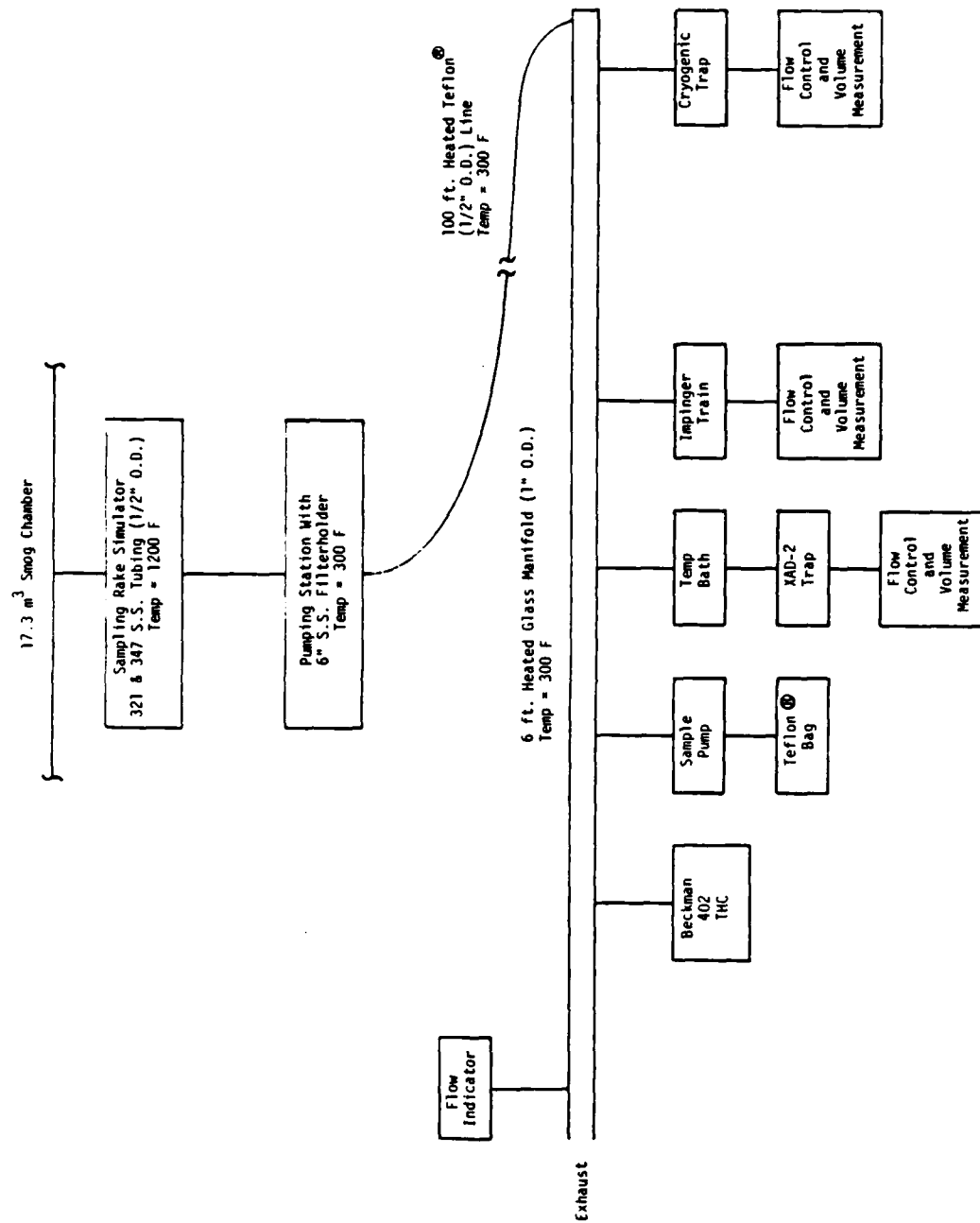


Figure 1. Sampling System for Task 1 Validation Experiments

TABLE 1. TEST COMPOUNDS FOR METHOD VALIDATION

Compound	Collection Technique
Methanol	GC*
Ethanol	GC*
Ethane	Cryogenic
Ethene	Cryogenic
Acetylene	Cryogenic
Propene	Cryogenic
Propane	Cryogenic
2-Methyl propane	Cryogenic
n-Butane	Cryogenic
2-Methyl butene-2	Cryogenic
Trans-2-butene	Cryogenic
n-Pentane	Cryogenic
2-Methyl pentane	Cryogenic
Cyclohexane	Cryogenic
Benzene	Cryogenic
Toluene	Cryogenic
m-Xylene	Cryogenic
p-Ethyl toluene	Cryogenic
1,2,4-Trimethylbenzene	Cryogenic
Dodecane	Cryogenic
Tetradecene	XAD
Hexadecane	XAD
Naphthalene	XAD
Anthracene **	XAD
Chrysene **	XAD
Benzo(a)pyrene **	XAD
Benzo(e)pyrene **	XAD
Coronene **	XAD
Formaldehyde	DNPH/HPLC
Acetaldehyde	DNPH/HPLC
Acrolein	DNPH/HPLC
Benzaldehyde	DNPH/HPLC/Cryogenic
2,4,6-Trimethylpyridine	XAD

* Analyzed by direct injection GC with photoionization detector.

** Spiked directly onto XAD.

TABLE 2. CONDITIONS OF VALIDATION EXPERIMENTS

Simulated Engine Condition	Idle	Idle	Idle	High Thrust	High Thrust	High Thrust
Sample Probe Temperature, F	1000	1000	800	1000	1000	1000
Relative Humidity, percent	57	55	54	54	51	50
Total Hydrocarbon, ppmC	68.0	54.0	43.0	19.8	16.2	12.5
NO _x , ppm	20.0	15.7	12.4	100.0	82.0	59.0
CO, ppm	750	590	464	37.0	30.0	22.0

A. CHAMBER VERSUS MANIFOLD SAMPLING

During the comprehensive validation experiments, samples were collected directly from the chamber and compared with those obtained through the heated stainless steel probe, pump, sample line, and manifold. Table 3 illustrates the results during idle conditions. The data indicate good agreement between the chamber and manifold samples and suggest that the sampling scheme does not introduce any artifacts or other forms of bias into the analytical results.

For comparison purposes, the data gathered during the validation experiments have been corrected to account for the chamber dilution rate effect resulting from the pump operation. A dilution rate of 24 percent/hour has been determined by measuring the loss of CO during the chamber validation experiments. This experimental value is identical to that rate determined by comparing the pump exhaust flow with the chamber internal volume.

Figures 2, 3 and 4 show the chromatograms obtained during the above comparison.

B. RECOVERY EFFICIENCIES FOR THE ENGINE SIMULATION EXPERIMENTS

Recovery efficiencies during the engine simulation experiments are given in Table 4. During idle conditions, two samples were collected at a probe temperature of 1000°F. The probe temperature was then lowered to 800°F and a third sample was collected. The same procedure was followed during the high-thrust experiments.

TABLE 3. DATA DEMONSTRATING SAMPLING SYSTEM TRANSFER EFFICIENCY

Compound	Analytical Method	Concentration ppbC	
		Chamber (inlet)	Manifold (outlet)
Ethane	Cryogenic/g.c.	2995*	2860*
Ethylene			
Acetylene			
Propene		369	359
Propane		516	503
i-Butane		402	390
n-Butane		1900	1850
t-2-Butene		637	607
c-2-Butene		164	141
i-Pentane		1780	1700
n-Pentane		765	733
i-Hexane		502	507
Benzene		511	512
Cyclohexane		510	513
Toluene		610	614
m-Xylene		672	677
p-Ethyltoluene		699	701
1,2,4-Trimethylbenzene	XAD/g.c.	718	721
2,4,6-Trimethylpyridine		464	432
Naphthalene		749	704
Dodecane		918	836
1-Tetradecene	DNPH/l.c.	1064	975
Hexadecane		1088	1018
Formaldehyde	Cryogenic/g.c.	172	211
Acetaldehyde		273	198
Acrolein		130	167
Benzaldehyde		670	470
Benzaldehyde		640	710

* Data obtained from capillary g.c. i.e. C₂'s not separated.

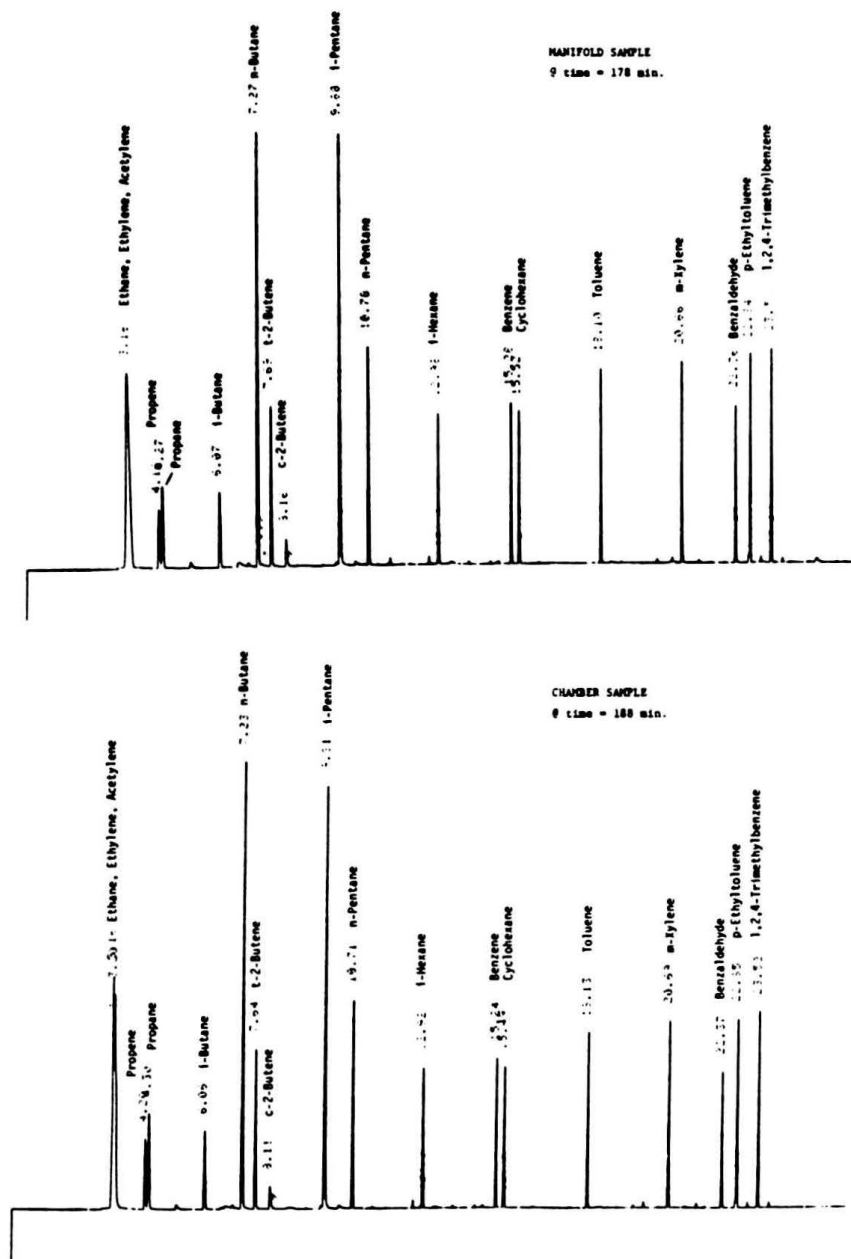


Figure 2. Chromatograms Obtained by Cryogenic Techniques (Capillary Column) Demonstrating the Transfer Efficiency of the Sampling System

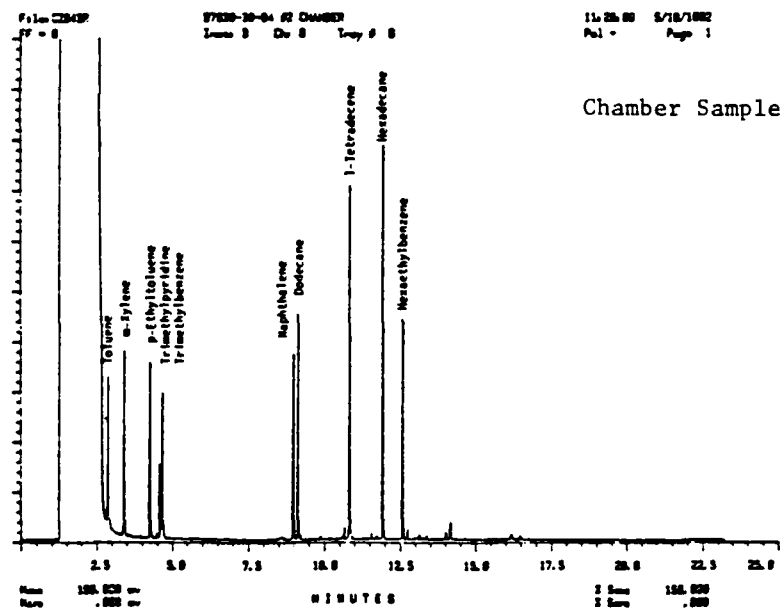
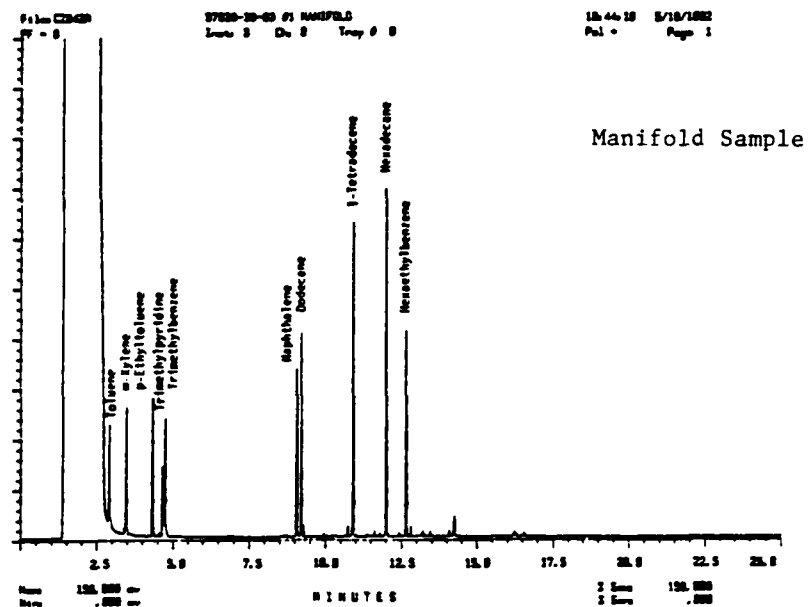


Figure 3. Chromatograms Obtained by XAD Techniques Demonstrating the Transfer Efficiency of the Sampling System

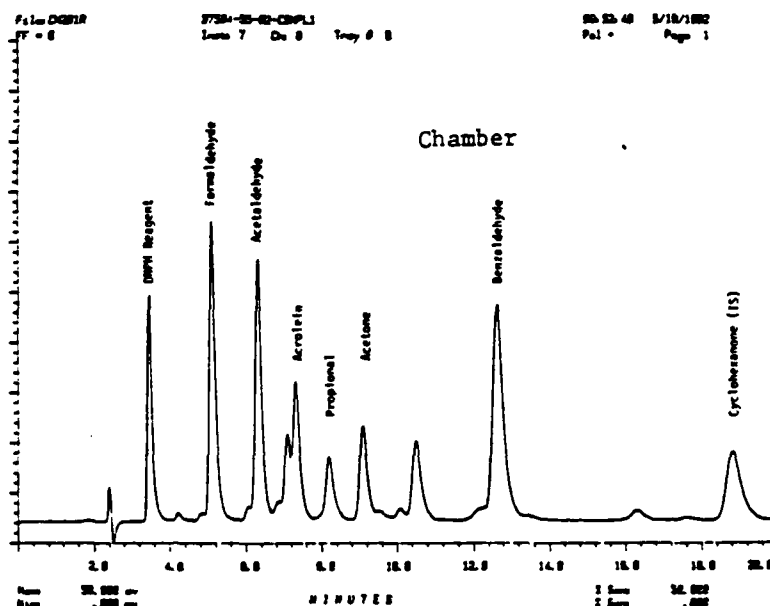
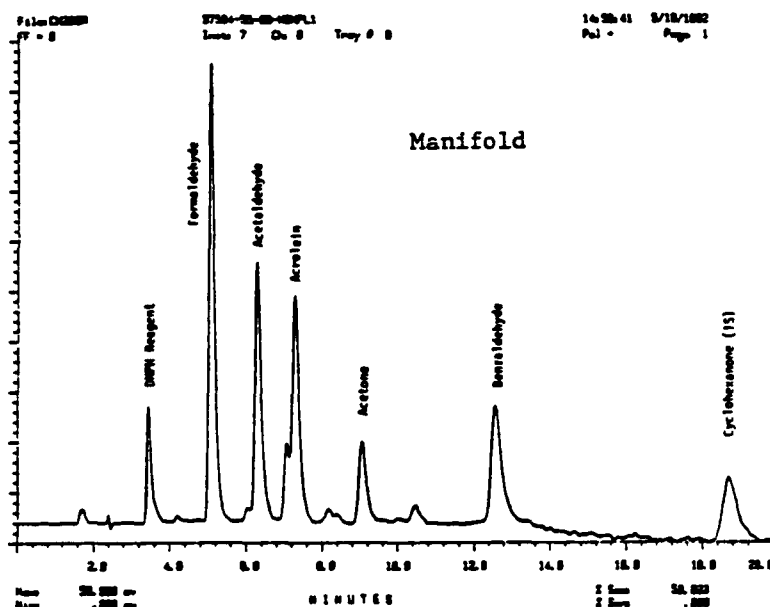


Figure 4. Chromatograms Obtained by DNPH Aldehyde Techniques
 Demonstrating the Transfer Efficiency of the Sampling System

TABLE 4. RECOVERY EFFICIENCIES FOR ENGINE SIMULATION EXPERIMENTS, BY PERCENT

Compound	Analytical Method	Idle		High Thrust	
		Probe @ 1000°F(a)	Probe @ 800°F	Probe @ 1000°F(a)	Probe @ 800°F
Ethane	Cryogenic/g.c.	92	100	97	(d)
Ethylene		91	101	93	(d)
Acetylene		93	100	94	(d)
Propene		104	108	98	102
Propane		104	110	109	102
i-Butane		102	100	109	100
n-Butane		100	100	100	100
t-2-Butene		111	108	110	102
c-2-Butene		100	106	106	107
i-Pentane		103	101	102	102
n-Pentane		103	102	108	101
i-Hexane		96	101	100	100
Benzene		98	102	102	100
Cyclohexane		98	103	100	100
Toluene		98	103	102	102
m-Xylene		94	99	99	99
p-Ethyltoluene		88	92	91	93
1,2,4-Trimethylbenzene		90	94	94	96
2,4,6-Trimethylpyridine	KAD/g.c.	80	(b)	43	(b)
Naphthalene		82	81	88	100
Dodecane		88	96	98	91
1-Tetradecene	DNPH/l.c.	70	68	81	82
Hexadecane		56	55	90	82
Formaldehyde		17 ^(c)	7 ^(c)	113	110
Acetaldehyde		70	65	90	98
Acrolein		60	58	62	65
Benzaldehyde		57	67	58	78

(a) Average of two experiments.

(b) Not determined because of instability in chamber (see text).

(c) Formaldehyde data for idle condition is not representative because of a suspected weighing error in loading the chamber.

(d) Integration problem with C₂ hydrocarbon gas chromatograph.

The compound recovery efficiency is determined by comparing the amount of material recovered in the sample to the amount of material originally injected into the chamber. The theoretical concentrations are based upon a chamber volume of 17.3 m³. Table 4 reflects the degree of accuracy in determining the concentrations of the test matrix. Very acceptable recoveries were obtained. The data gathered by the cryogenic technique show recoveries between 95 and 105 percent. The XAD-2 method resulted in recoveries of 80 percent or better, while the aldehyde method averaged about 60 percent recovery.

The concentrations of compounds determined by more than one method are compared in Table 5. In general, good agreement was found between the XAD-2 and the cryogenic collection methods. The abnormally high p-ethyltoluene values obtained with the XAD-2 technique during idle operation were probably due to contamination during the extraction process. The subsequent thrust tests showed very good agreement between methods. The benzaldehyde comparisons show relatively large deviations between methods. The discrepancy is due to the low (~60 percent) recovery of benzaldehyde by the DNPH method.

Recovery data for the PAHs are shown in Table 6. Known amounts of these compounds were placed directly in the XAD-2 sampling device and subjected to the simulated exhaust streams to assess chemical stability during the sampling process. Again, very acceptable recoveries were obtained.

C. PRECISION CHECK

To determine the precision of the analytical methods, the average concentrations were calculated for the idle experiments, as shown in Table 7. From this data base, a percent relative standard deviation was calculated for each compound. Except for benzaldehyde (using the DNPH method), all the test compounds have RSD values of less than 10 percent.

The analytical method for alcohol analyses involved the use of a gas chromatograph/photo-ionization detector system (8). The sensitivity of this unit allowed for direct injection (2 cc) of gas samples and provided low ppb-level detection of methanol and ethanol. However, the GC unit has no column oven capability and thus essentially operates at room temperature. This restriction severely limited possible column types that would adequately separate the two alcohols from the remaining organics in

TABLE 5. COMPARISON OF COMPOUNDS THAT OVERLAP THE ANALYTICAL METHODS

Compound (ppbC)	Idle			High Thrust		
	XAD-2 (a)	Cryo (b)	% RSD	XAD-2 (a)	Cryo (b)	% RSD
m-Xylene	2685	2660	<1	757	632	13
p-Ethyltoluene	4457	2800	32	738	668	7
1,2,4-Trimethylbenzene	2935	2890	1	712	717	<1
	DNPH (a)	Cryo (b)	% RSD	DNPH (a)	Cryo (b)	% RSD
Benzaldehyde	1977	2830	25	467	677	26

(a) Average of 3 runs.

(b) Average of 4 runs.

TABLE 6. RECOVERY DATA FOR PAHS SPIKED ON XAD TRAPS PRIOR TO SAMPLING^(a)

Compound	Idle			High Thrust			Process Spike (no air sampled)		
	Amount Spiked, µg	% Recovery	% RSD	Amount Spiked, µg	% Recovery	% RSD	Amount Spiked, µg	% Recovery	% RSD
Anthracene	20	105	12.0	10	76	28	10	102	17.0
Chrysene	20	86	4.2	10	104	16	10	91	5.0
Benzo(e)pyrene	20	102	1.5	10	120	17	10	102	1.4
Benzo(a)pyrene	20	89	12.0	10	90	22	10	92	6.7
Coronene ^(b)	20	92	9.5	-	-	-	-	-	-

(a) Triplicate samples collected at each operating condition.

(b) Compound not available during Task 1. It was spiked onto XAD traps and exposed to combustor rig exhaust during Task 2 testing.

TABLE 7. PRECISION DATA FOR ENTIRE SAMPLING AND ANALYSIS SYSTEM

Compound	Analytical Method	Number of Determinations	Average Concentrations Found ppbC	% RSD
Ethane	Cryogenic/g.c.	4	700	2.1
Ethylene		4	1220	3.0
Propene		4	508	1.6
Acetylene		4	980	2.7
i-Butane		4	390	3.1
n-Butane		4	1560	5.4
Propene		4	379	4.1
i-Pentane		4	1320	2.1
n-Pentane		4	705	1.8
2-Methylpentane		4	498	1.5
Benzene		4	504	1.9
Cyclohexane		4	504	1.9
Toluene		4	597	1.9
m-Xylene		4	632	8.7
p-Ethyltoluene		4	668	8.8
1,2,4-Trimethylbenzene		4	717	2.2
Naphthalene		4	761	4.9
Dodecane	XAD/g.c.	3	836	5.8
1-Tetradecene		3	976	3.8
Hexadecane	--	3	1020	6.1
2,4,6-Trimethylpyridine ^(a)		--	--	--
Formaldehyde	DNPH/l.c.	3	212	9.7
Acetaldehyde		3	198	9.0
Acrolein		3	167	7.2
Benzaldehyde		3	467	24.0

(a) Precision for this compound could not be determined because of rapid loss from chamber.

the validation mixture. During the comprehensive validation experiments, methanol and ethanol data were not available because of hydrocarbon overlap on the GC columns tested. Subsequent to the laboratory tests, a 6-foot column containing 0.2 percent Carbowax 1500[®] on Carbopack C[®] was obtained and exhibited good separation characteristics for the alcohols. Further testing of this column type was conducted during the Task 2 field study.

D. CARBON BALANCE

For purposes of the Task 1 validation experiments, a carbon balance was defined as the ratio of the sum of all individual organics measured in the environmental chamber sample divided by the total hydrocarbon concentration as measured by a heated-probe flame ionization THC monitor. Because the total hydrocarbon monitor responds on a ppmC (part per million carbon) basis, all individual components must be converted to ppmC for comparison. Herein lies a problem. For species other than simple hydrocarbons, such as oxygenated organics, the FID detector response is generally less than 1.0 per carbon atom. For the validation compounds, the individual response factors are known, but during Task 2 and 3 experiments the exact response factors for many of the species will not be known. To make the Task 1 carbon balances as realistic as possible, we assumed that the exact FID response factors for oxygenated organics are unknown. During Tasks 2 and 3, total hydrocarbon data both from FID monitors and from EPA Method 25 will be available. In theory, the latter method yields equivalent response from each carbon atom regardless of molecular structure (9). To compare with the two total hydrocarbon procedures, i.e. FID and Method 25, we will convert oxygenated compounds from ppm-compound to ppm-carbon in two ways. In the first, we have assumed quantitative response (i.e., 1.0) from each carbon atom in the molecule; in the second we assumed that each oxygen atom eliminates the response of one carbon atom. For example, by the second procedure, formaldehyde does not get counted for carbon balance purposes, and only six of the seven benzaldehyde carbon atoms are counted. A detailed example of carbon balance by the first procedure is shown in

Table 8 for an experiment simulating engine idle. The sum of the individual species is 51.21 ppmC, while the total hydrocarbon monitor yielded 54.0 ppmC. Thus, a 95-percent carbon balance was achieved. For this same example, if one calculates the species sum using concentrations adjusted for the FID response of oxygenates, as described above, the carbon balance is still 94 percent. The carbon balances for the six comprehensive validation experiments listed in Table 2 are presented in Table 9. Both methods of dealing with response factors are included. The results assuming "total carbon" response are followed by the "FID" response data in parenthesis. The carbon balances range from 90 to 97 percent. Carbon balances in this range are considered to be completely satisfactory and consistent with the goals of this program. The missing carbon, or carbon deficit, is undoubtedly caused by the fact that, (1) quantitative data are lacking for trimethylpyridine, methanol and ethanol, three compounds known to be present in the experimental organic mix, and (2) the XAD and DNPH data have not been adjusted to account for the sample recovery efficiencies, which are known to be less than 100 percent. These two factors were discussed earlier in this section.

TABLE 8. EXAMPLE CARBON BALANCE CALCULATION (ASSUMES RESPONSE FACTOR OF 1.0 FOR ALL CARBONS)

Compound Identified	Concentration, ppmC
methane	1.70
ethane	2.08
ethylene	3.68
propane	1.49
acetylene	2.89
i-butane	1.11
n-butane	4.70
propene	1.16
i-pentane	4.01
n-pentane	2.10
t-2-butene	1.76
c-2-butene	0.15
2-methylbutene-2	0.61
2-methylpentane	1.44
benzene	1.47
cyclohexane	1.47
toluene	1.72
m-xylene	1.89
p-ethyltoluene	1.97
2,4,6-trimethylpyridine	0.67
1,2,4-trimethylbenzene	2.02
naphthalene	2.02
dodecane	2.47
tetradecene	2.20
hexadecane	2.02
formaldehyde	0.11
acetaldehyde	0.41
acrolein	0.54
benzaldehyde	1.45
	<u>51.31</u>
Total Hydrocarbon (FID)	54.0
Carbon Balance ($\frac{\sum \text{species}}{\text{THC}}$)	95%

TABLE 9. CARBON BALANCES FOR SIX VALIDATION EXPERIMENTS

Experiment No.	Idle Conditions			High Thrust Conditions		
	1	2	3	1	2	3
Total Hydrocarbon Concentration, ppmC	68.0	54.0	43.0	19.75	16.25	12.50
Sum of Measured Species, ppmC	61.94 ^(a) (61.08) ^(b)	51.31(50.59)	41.86(41.33)	18.79(18.06)	15.17(14.54)	11.84(11.39)
Carbon Balance, %	91(90)	95(94)	97(96)	95(91)	93(90)	95(91)

(a) Assumes response factor of 1.0 for each carbon.

(b) Assumes each oxygen eliminates response of one carbon.

SECTION III

TASK 2. COMBUSTOR RIG STUDIES

In the overall scheme of this project, Task 2, is a preliminary test of the sampling and analysis systems developed in Task 1 prior to full-scale turbine engine testing in Task 3. In addition to providing a realistic test of the systems, however, the results of combustor rig experiments are expected to provide valuable information which will be used to assess the suitability of combustor rigs as surrogates for turbine engines and also provide information on exhaust composition and reactivity which will assist us in preparing for the Task 3 engine tests and Task 4 photochemical reactivity studies.

The combustor rig experiments were conducted at the GE Advanced Combustion Laboratory at Evendale, OH using a one-sixth sector of the annular combustor from a TF-39 engine. Tests were conducted using JP-5 fuel with the combustor at idle. The remainder of this report describes the experimental procedures, results and analysis of the combustor rig experiments.

A. EXPERIMENTAL

The Evendale field experiments were conducted over a 2-week period and included 4 days of actual combustor rig test runs. During this period our research effort focused on three tasks:

- Exhaust sampling
- Biological assay sampling
- Fuel sampling

The experimental aspects of these tasks, along with descriptions of GE's combustor test facility and Battelle's mobile laboratory, follow.

1. Combustor Test Facility

The Advanced Combustion Laboratory is designed and equipped to accommodate a variety of experimental investigations of moderately sized combustion systems. An important use of this test facility in recent years has been in emissions reduction programs.

During this program, 100 psig shop air was supplied and supplemented with air from a central supply system to maintain flow rates of 4 to 5 lbs/sec through the combustor rig. An indirect-fired preheater was used to provide nonvitiated air to simulate compressor discharge temperature. JP-5 fuel was supplied from holding tanks at the laboratory site.

Air and gas flows were metered by ASME standard thin-plate orifice meters. A variety of interchangeable orifice plates and manometer fluids were maintained to enable accurate measurement of a wide range of flows. Fuel flows were metered by turbine-type flow meters, whose signals were input to an Apple computer system. Thermocouple readouts and fluid pressures were also recorded by the same computer system.

The low-pressure 60° sector TF-39 combustor test rig is shown in Figure 5. The rig contains five fuel nozzles as compared with 30 fuel nozzles in the engine. The combustor housing was constructed from a segment of a TF-39 engine compressor rear frame and seal bearing assembly, so that it exactly duplicated the engine combustor flow path. However, due to its overall construction, this rig could not be run to pressures simulating high-power engine conditions, but was ideally suited for simulation of idle conditions.

Four gas sample rakes were used in the test rig. Each rake contained five (S.S.) orifices, 1.3 mm diameter. The sample from each rake could be measured individually, or the four rakes could be manifolded for a combined sample. During this study all rakes and connecting lines were steam-cooled in order to quench the hot exhaust gases.

The combustor rig experiments also made use of a General Electric emissions analysis package for monitoring CO, CO₂, NO/NO_x, total hydrocarbons and Smoke Number. The four gas analyzers in this system were manufactured by Beckman Instruments, Inc. The CO (Model 865) and CO₂ (Model 864) analyzers were nondispersive infrared instruments. The NO/NO_x analyzer was a Model 951 heated chemiluminescence analyzer with thermal converter, and the HC analyzer was a Model 402 flame ionization instrument. Figure 6 illustrates this instrumentation package.

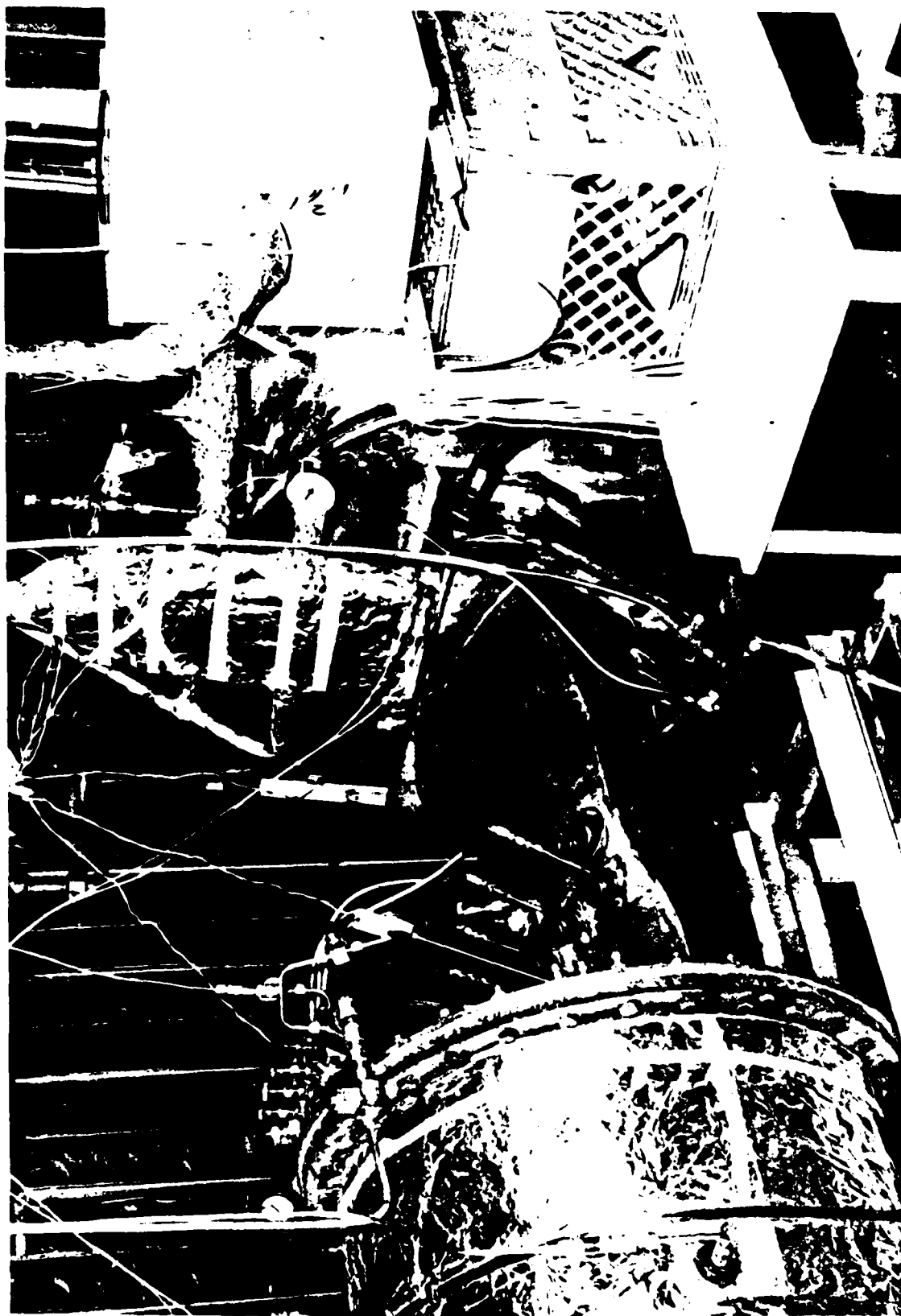


Figure 5. One-Sixth Sector Combustor From TF-39 Turbine Engine



Figure 6. Continuous Emissions Analyzers Associated With Combustor Rig Facility

Two standard relay racks housed the four gas analyzers along with readout devices, flow meters, flow control valves, and solenoid-operated calibration gas valves. Two double-pen recorders provided a permanent and continuous record of the instrument outputs, while the actual test values were more quickly read and conveniently stored on computer. The smoke measurement console was a General Electric-designed system and conformed to both EPA requirements and SAE ARP 1179A procedures.

The gaseous emissions analyzers were calibrated with certified mixtures of propane in air, CO and CO₂ in nitrogen, and NO in nitrogen. Each analyzer was calibrated with four separate mixtures in concentrations such as to cover the range of concentrations of gas samples from the test. Each calibration gas was certified by the vendor to an accuracy of 2 percent of the concentration. In addition, the calibration gases were compared at General Electric with Standard Reference Material (SRM) mixtures which were obtained from the National Bureau of Standards and were certified accurate within 1 percent. A complete calibration was performed daily.

2. Mobile Laboratory

A 30-foot trailer served as Battelle's laboratory during the 2-week field study. Figure 7 shows the mobile lab positioned next to the combustor rig facility. The lab is wired for 100-ampere service and contains two air-conditioning units for adequate temperature control. The trailer is also equipped with facilities for preparing and recovering samples. Sufficient space exists for a variety of continuous gas and particle monitors. The operational procedures and instrumentation employed in this field study are provided below.

3. Exhaust Sampling

The exhaust testing experiments were conducted June 23, 24, 30 and July 1. A schematic of the sampling system used during these tests is shown in Figure 8 (Figure 5 depicts the actual combustor unit used along with several key components). During normal operation the combustor rake inlet pressure was maintained at 48 psia. At this pressure, adequate flow to both GE's and Battelle's instrumentation could be achieved by adjusting

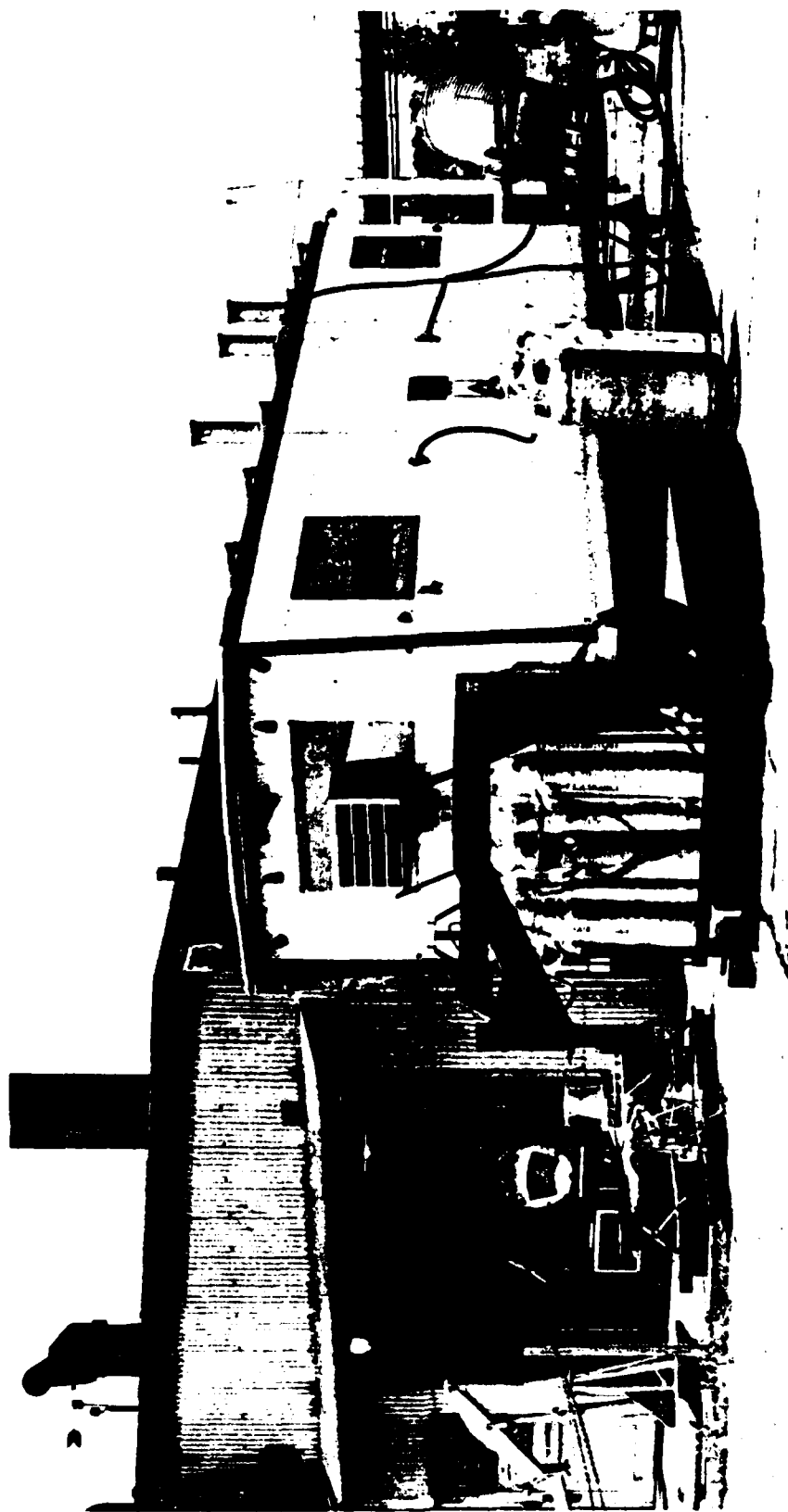


Figure 7. Mobile Laboratory Located Adjacent to Combustor Rig Facility

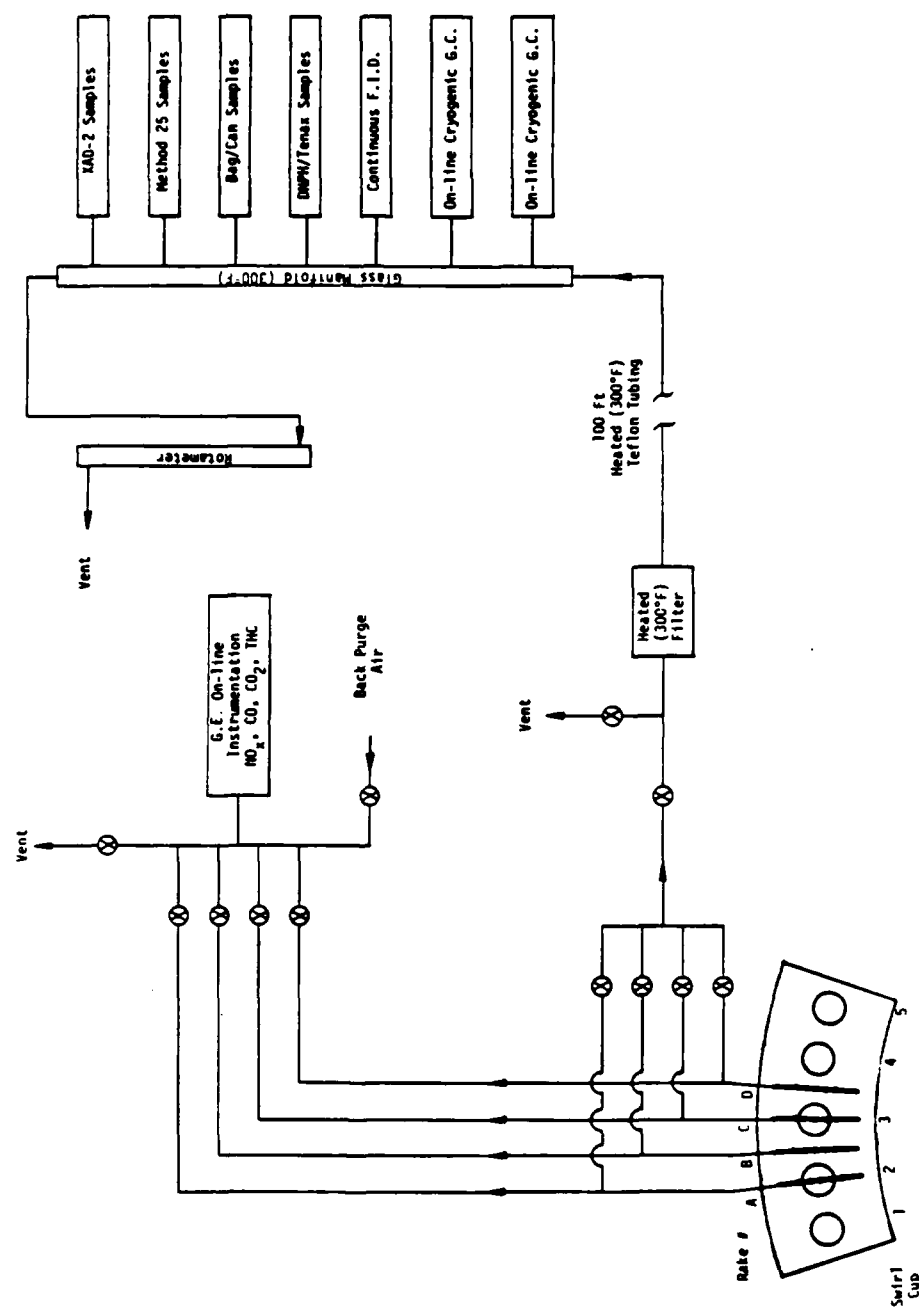


Figure 8. Schematic of Combustor Rig and Sampling System

the appropriate vent valves shown in the figure. Additionally, all sampling lines, connections, etc., were heated to 300°F to prevent water condensation and minimize sample adsorption losses.

a. Experimental Sequence

A typical experiment was carried out as follows:

(1) House-compressed air was turned on, preheated to 300°F, and directed through the combustor rig. A Pallfax[®] quartz fiber filter was placed in the filter housing and all sampling apparatus, connectors, etc., were then heated to 300°F. During the combustor rig temperature equilibration period, all necessary instrumentation span and zero checks were completed.

(2) When the system had equilibrated, an initial set of samples (background) was collected for organic characterization of the compressor air.

(3) The sampling rake was then back-purged with instrument air to prevent rake contamination by fuel and the rig ignition was turned on. Following rig startup, the rake was again opened and monitored with the total hydrocarbon analyzers. After rig equilibration, three additional sequential test runs were performed. Each test run required 35 minutes to complete. During this period, close coordination between GE and Battelle personnel was required in an effort to maintain constant exhaust emission levels. This concern was critical since the sampling duration of several of the methods was less than 35 minutes. Table 10 lists the rates for each method. Following each 35-minute test run, a 1-quart fuel sample was obtained. At the end of the day a 1-gallon sample was procured from the holding tank.

b. Cryogenic On-Line Gas Chromatograph

A Hewlett-Packard Model 5880 gas chromatograph with micro-processor control and integration capabilities provided on-line data gathering during the combustor rig tests. Battelle's technique involved the passage of a specific volume of air (usually 30 cc) through a freeze-out sample loop (15 cm long by 0.2 cm I.D. stainless steel tubing) filled

TABLE 10. SAMPLING TECHNIQUES AND PARAMETERS DURING COMBUSTOR RIG TESTS

Sampler	Sampling Rate, lpm	Sampling Duration, Min	Total Sample Volume, l	Samples/Test Day
Cryogenic	0.030	1	0.030	4
Tenax	1	0.2-2	0.2-2	1
XAD-2	28	35	980	4
Bags/Cans	1	5	5	4
DNPH	1	20	20	4
Method 25	0.05-0.10	35	1.75-3.5	4
THC Analyzer	Continuous			
General Electric Analyzers	Continuous			
THC	Continuous			
CO	Continuous			
CO ₂	Continuous			
NO/NO _x	Continuous			

with 60/80 mesh silanized glass beads. Sampling was initiated by immersing the loop into a dewar of liquid argon (-186°C) and collecting a known volume of air. Injections were accomplished by transferring the collected sample from the loop through a Carle six-port valve and onto the analytical column. The components in the loop were then flash evaporated into the gas chromatograph by rapidly heating a thermocouple wire which was wound around the sampling loop.* During normal operations the trap system was heated from liquid argon temperature to 150°C within 20 seconds.

The GC was equipped with two flame ionization detectors. The C_2 through C_5 hydrocarbons were resolved with a 6-meter by 0.2-centimeter I.D. column packed with phenylisocyanate on 80/100-mesh Porasil[®] C. The column was housed in an oven external to the GC and oven operation at 45°C provided adequate resolution of these species. A 50-meter OV-1 wide-bore fused silica column (Hewlett-Packard) was used to separate the C_4 through C_{10} organics. Optimum results in component resolution were achieved by temperature programming from -50 to 150°C at $8^{\circ}/\text{minute}$. This two-column analytical approach was necessary to adequately resolve the major C_2 to C_{10} organic species. The overlap in peak detection capabilities (C_4 through C_5 hydrocarbons) when using this two-column approach provided a good means of internally cross-checking the system.

Sampling for both traps was initiated at the same time and samples were collected for 2 minutes. The sample line for the C_4 through C_{10} organics was maintained at 150°C ; the sample line for the C_2 to C_5 organics was unheated. The sample lines and trap units were heated and back-flushed with zero grade N_2 after each test run.

Calibration of the gas chromatographic systems was accomplished by injecting an external standard mixture into each GC. A ppbC response was determined and the value obtained was then assigned to all identified and unidentified compounds (i.e., 1 ppbC propane responds the same as 1 ppbC hexane, etc.). The standard mixtures are cross-checked with several NBS traceable "propane in air" standards.

* A hot water dewar was used for the C_2 to C_5 analyses.

Bag samples were immediately analyzed for methanol and ethanol content; the can samples were returned to the Battelle laboratory for methane and carbon monoxide determination.

The methanol and ethanol analyses were accomplished with a Photovac Model 10A10 portable photo-ionization gas chromatograph. This unit operates at room temperature with a 1.8-meter by 0.2 cm I.D. stainless steel column containing 0.2 percent Carbowax[®] 1500 on Carbopack[®] C.

Calibration was accomplished by injecting known amounts of the alcohols (liquids) into 10-liter bags. Detection of 10 ppb ethanol and 50 ppb methanol was achieved when directly sampling 2 cc of air.

Methane and carbon monoxide concentrations were determined by transporting the canister samples to the Battelle laboratory, where a Beckman 6800 GC performed the separation and quantitation steps. A multi-point calibration, daily span and zero checks were performed, using NBS traceable methane and carbon monoxide standards.

f. Method 25

EPA Method 25 (9) was performed by PEDCo Environmental Company. PEDCo collected the organics by withdrawing samples through a condensate trap (dry ice) into an evacuated tank (10 liters). Once collected, the samples were transferred to the PEDCo laboratory where the trap contents were oxidized to CO₂, reduced to methane, and determined by FID. The organic contents of the tank were determined in the same manner after GC separation of CO, CO₂, and CH₄. The primary advantage of Method 25 is that all of the organics are determined as methane, and hence, compound-to-compound variability in FID response is not a problem.

g. Tenax[®] Samples

During the field tests several Tenax[®] traps were collected, returned to Battelle, and thermally desorbed for GC/MS compound identification. These samples were processed with the same GC column used in the field study and, as a result, positive identification was possible for many of the peaks eluting from the on-line cryogenic gas chromatograph.

Prior to field sampling, the Tenax[®] traps were cleaned by purging with high-purity helium at 300°C. During sampling, volumes of 0.2 to 2 liters of exhaust (cooled to ~80°F) were collected through the Tenax[®] cartridges (1.5 grams).

h. XAD-2 Samples

XAD-2 samples were used to quantify C₁₀ through C₁₇ hydrocarbons and polycyclic aromatic hydrocarbons PNA. During the field program a 22-gram portion of XAD resin (prepurified by methylene chloride extraction) was placed in a sampling tube thermostated at 130°F, using a constant temperature bath. The exhaust samples were collected at a rate of 1 cfm for 35 minutes to collect a total volume of 1 m³. After collection the trap/condensor assembly was capped with glass connectors and transported to the laboratory for analysis.

The XAD-2 resin cartridges were extracted within 24 hours after collection. The resin was extracted (Soxhlet[®]) for 16 hours with methylene chloride. The extract was spiked with 500 µg of hexaethylbenzene (HEB) and 10 µg of each of the following deuterated PNAs; D₈-naphthalene, D₁₀-phenanthrene, D₁-chrysene, and D₁₂-benzo(a)pyrene (BAP). HEB was used as an internal standard for GC/FID quantification of hydrocarbons whereas the deuterated PNAs were used as internal standards for GC/MS quantification of PNAs.

The solvent extract was then concentrated to 50 mL using a Kuderna-Danish (K-D) concentrator and analyzed by GC/FID. The relatively large final volume (50 ml) was employed because of the large quantity of hydrocarbons present in the exhaust.

The GC/FID analysis conditions employed were as follows:

- GC - Carlo Erba Model 2160
- Column - 50 meter SE-54 cross-linked fused silica. HP
- Carrier Flow - H₂ @ 50 cm/sec
- Injector/Detector Temperature - 275°C
- Temperature Program - Inject at room temperature and increase to 50°C after 1 minute; hold isothermal at 50°C for 1 minute; then 50-250 at 6°/minute.
- Injection - 2 µl splitless, split on at 45 seconds.

Data were acquired and processed on a Computer Inquiry Systems chromatographic data system and all raw data was archived on nine-track magnetic tape. The GC system was calibrated using a calibration standard containing 63 µg/ml of each normal paraffin from n-C₉ to n-C₁₆ and 50 µg/ml of HEB. All data were reported as ppmC, using the response factor of HEB for all components except the normal paraffins for which specific response factors were determined.

One extract (Test 15), as well as the JP-5 fuel from that test, was analyzed by GC/MS in the full-spectrum scan mode (40-500 AMU) using the same conditions as for GC/FID. Helium, rather than hydrogen carrier gas, was used since the GC/MS system could not accept hydrogen.

i. PNA Analysis

Selected XAD extracts were analyzed for PNAs using a GC/MS isotope dilution procedure. The extract was concentrated and exchanged into cyclohexane (final volume, 1 ml).

Davidson Grade 923 (100-200 mesh) silica gel was rinsed with methanol and activated in an oven at 130°C for 24 hours. Ten grams of activated silica gel was placed in 40 ml of methylene chloride and the suspension poured into a 1 cm x 25 cm chromatographic column. The column was eluted with 40 ml of hexane.

The cyclohexane solution (XAD extract) was placed on the silica gel column, rinsing the sample container with an additional 2 ml of cyclohexane. The column was then sequentially eluted with 25 ml of hexane (Fraction 1), benzene (Fraction 2), and methanol (Fraction 3). These fractions will contain aliphatic/olefinic hydrocarbons, aromatic hydrocarbons, and polar substituted compounds, respectively.

The benzene fraction was concentrated to 1 ml and analyzed for PNAs using GC/MS in the multiple ion detection (MID) mode. A Finnigan 3200 GC/MS system, operating with an INCOS data system, was used. A 30-meter SE-52 glass capillary column and helium carrier gas were used. The temperature program was from 50 to 300°C at 6°/minute and columns were held at 300°C until no more material eluted (approximately 15 minutes).

Ions monitored were as follows: m/e 128 (naphthalene), m/e 136 (D_8 -naphthalene), m/e 142 (methyl naphthalenes), m/e 156 (dimethylnaphthalenes), m/e 178 (phenanthrene/anthracene), m/e 188 (D_{10} phenanthrene), m/e 202 (pyrene/fluoranthene), m/e 212 (D_{10} pyrene), m/e 228 (chrysene/benzanthracene), m/e 240 (D_{12} -chrysene), m/e 252 (benzopyrenes/benzofluoranthenes/perylenes), m/e 264 (D_{12} -benzo(a)pyrene). The methyl and dimethylnaphthalenes were quantified using the response factor for D_8 -naphthalene, whereas all other compounds were quantified using the corresponding deuterated PNA.

The GC/MS system was calibrated each day using a standard containing 1 μ g/ml of each native PNA, and 10 μ g/ml of each deuterated PNA. A fuel sample was also analyzed for PNAs by processing 250 μ l of fuel dissolved in 1 ml of cyclohexane through the silica gel cleanup procedure described for XAD samples.

One methanol fraction (from Test 14) was analyzed for polar PNAs using the same GC/MS conditions except that full-spectrum scan (40-500 AMU), rather than MID, was employed.

4. Biological Assay Sampling

Following the completion of Test 6, BCL's sampling line was disconnected from the manifold and reconnected to an XAD-2 (150 grams) sampling assembly. Meanwhile, a preweighed filter was positioned in the filter holder. The filter holder and 100-foot Teflon[®] line were maintained at 300°F, while the XAD-2 condenser was cooled to 140°F. By readjusting the vent valve, a flow rate of 5 cfm was established and a total volume of 27 m³ was passed through the filter and XAD-2 system.

Following collection, the filter and XAD-2 samples were transferred to the laboratory (including blanks for both matrices) and were extracted with methylene chloride overnight. The extracts were concentrated to 0.5 ml, using a K-D concentrator, and placed in a conical centrifuge tube and 2 ml of DMSO were added. Methylene chloride was removed from the extract under vacuum at 75°C for 30 minutes using a vortex evaporator. The extracts were placed in screw-capped vials and stored at dry ice temperatures until analysis.

The XAD bioassay extract contained ~1.5 grams of residue (mostly unburnt fuel) and hence could not be concentrated below ~2 ml. Therefore, this extract was diluted to 5 ml with DMSO prior to shipment to the bioassay laboratory.

5. Fuel Sampling

As mentioned earlier, 1-quart fuel samples were taken after each test run. A portion of each sample was returned to BCL and analyzed by GC/FID. One hundred milligrams of fuel and 0.5 milligrams of HEB (hexaethylbenzene) were diluted to a total volume of 50 ml with methylene chloride. The fuel samples were analyzed in the same fashion as described previously for the XAD-2 samples.

Additionally, two 1-gallon fuel containers taken after Test Runs 4 and 16 were shipped to Wright-Patterson AFB for ASTM characterization tests. These standard procedures include the following:

- Simulated distillation (ASTM D2887)
- Hydrocarbon type analysis (ASTM D-2789-71)
- Average carbon number (ASTM D-2887)
- Density at -30°, 32°, 70° and 100°F
- Freezing point (ASTM D2386)
- Existent gum (ASTM D381)
- Luminometer number ASTM D1740 and smoke point (ASTM D1322)
- Viscosity (ASTM D445) at -30°, 32°, 70° and 100°F
- Total sulphur, weight percent (ASTM D1266)
- Aromatics, volume percent (ASTM D319)
- Olefins, volume percent (ASTM D1319)
- Distillation (ASTM D86)
- Hydrogen, weight percent (ASTM D3701).

B. RESULTS

The Task 2 combustor rig studies were conducted on June 23, 24, 30 and July 1, 1982. Fifteen tests were carried out, with a test defined as one 35-minute sampling period. Three tests were run on background air without the combustor rig operating. The remaining 12 tests involved exhaust sampling with the rig operating at idle on JP-5 fuel. The operating

conditions and emissions data for these 15 tests are presented in Table 11. This table summarizes the most important experimental conditions for the combustor rig tests.

Samples of the JP-5 fuel used for the combustor rig experiments were obtained during each test and analyzed by GC/FID. A representative chromatogram for the fuel for Test 8 is shown in Figure 9. The results of the chromatographic analyses of the fuels used in each test are presented in Table 12. Additional characterization of the fuel samples was performed by Major Don Potter of Wright-Patterson AFB. The results of these analyses are discussed later in this section.

During the combustor rig studies, exhaust samples were collected and analyzed by several methods in order to identify and quantify the organic species present in the exhaust. The sampling and analysis methods employed were those developed and validated in Task 1. Figures 10, 11 and 12 present examples of chromatograms for the three most comprehensive techniques. Figure 10 shows the chromatographic output from the cryogenic capillary column GC used for species in the C_2 - C_9 range. Figure 11 shows the results of GC-FID analysis of one of the XAD-2 adsorbent samples used to quantify C_{10} - C_{17} compounds. An HPLC chromatogram for an exhaust sample collected by DNPH method is included in Figure 12.

The results from these three procedures are shown for all 12 combustor rig tests in Table 13-21. Tables 13-16 show the cryogenic data, Tables 17-20 give the XAD results, and the DNPH data are included in Table 21. Figures 13 and 14 demonstrate the GC/photo-ionization detection results obtained for alcohols during Test 11.

PNA concentrations determined by GC/MS for selected tests are presented in Table 22. Analysis of the bioassay filter sample showed that the particle-bound concentration of any PNA never exceeded 2 percent of its gas phase concentration.

Another very important aspect of the Task 2 studies was collection of data on the total concentration of organics in the exhaust. Two Beckman 402 heated-probe FID total hydrocarbon analyzers were used for this purpose. The results from one of these instruments were summarized earlier in Table 11. However, the data reported by the second analyzer are actually the most

TABLE 11. ENGINE OPERATING CONDITIONS AND STANDARD EMISSIONS
DATA FOR COMBUSTOR RIG TESTS

	6/23/82				6/24/82			
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Inlet Air Temperature, °F		353	354	353		353	355	354
Atmospheric Pressure, Inches Hg		29.539	29.539	29.539		29.568	29.568	29.568
Relative Humidity, Inlet, %		5	5	5		5	5	5
Fuel Flow, lbs/hr		204	204	204		204	204	204
Air Flow, lbs/hr		1.66×10^4	1.66×10^4	1.66×10^4		1.66×10^4	1.66×10^4	1.66×10^4
Fuel/Air Ratio, Actual		.01229	.01229	.01229		.01229	.01229	.01229
Fuel/Air Ratio, Calculated		.01296	.01356	.01330		.01238	.01258	.01250
Combustion Efficiency, %		96.66	96.78	96.71		96.39	96.51	96.53
NO _x , ppm		29.4	29.9	30.1		28.9	28.5	28.5
NO, ppm		--	--	--		--	--	--
CO, ppm		788.0	775.5	759.7		739.1	741.8	736.0
CO ₂ , %		2.61	2.74	2.68		2.45	2.53	2.52
Smoke Number		--	--	--		--	--	--
Total Hydrocarbon, ppmC (GP)		543.8	531.3	548.4		555.9	557.6	550.8

	6/30/82				7/1/82		
	Test 9	Test 10	Test 11	Test 12	Test 14	Test 15	Test 16
Inlet Air Temperature, °F		354	355	354	352	355	353
Atmospheric Pressure, Inches Hg		29.313	29.313	29.313	29.577	29.577	29.577
Relative Humidity, Inlet, %		5	5	5	5	5	5
Fuel Flow, lbs/hr		204.5	204	204	204	204.5	203.9
Air Flow, lbs/hr		1.66×10^4	1.66×10^4	1.66×10^4	1.66×10^4	1.66×10^4	1.66×10^4
Fuel/Air Ratio, Actual		.01232	.01229	.01229	.01229	.01232	.01228
Fuel/Air Ratio, Calculated		.01260	.01275	.01228	.01210	.01236	.01233
Combustion Efficiency, %		96.76	96.60	96.76	96.95	96.99	96.90
NO _x , ppm		27.8	29.2	29.7	27.7	29.1	27.0
NO, ppm		8.8	9.8	9.4	9.0	9.9	9.2
CO, ppm		734.0	700.0	686	693	592	657
CO ₂ , %		2.54	2.46	2.46	2.44	2.51	2.49
Smoke Number		4.8	5.1	4.8	4.2	4.1	3.7
Total Hydrocarbon, ppmC (GP)		488	512	512	504	495	486

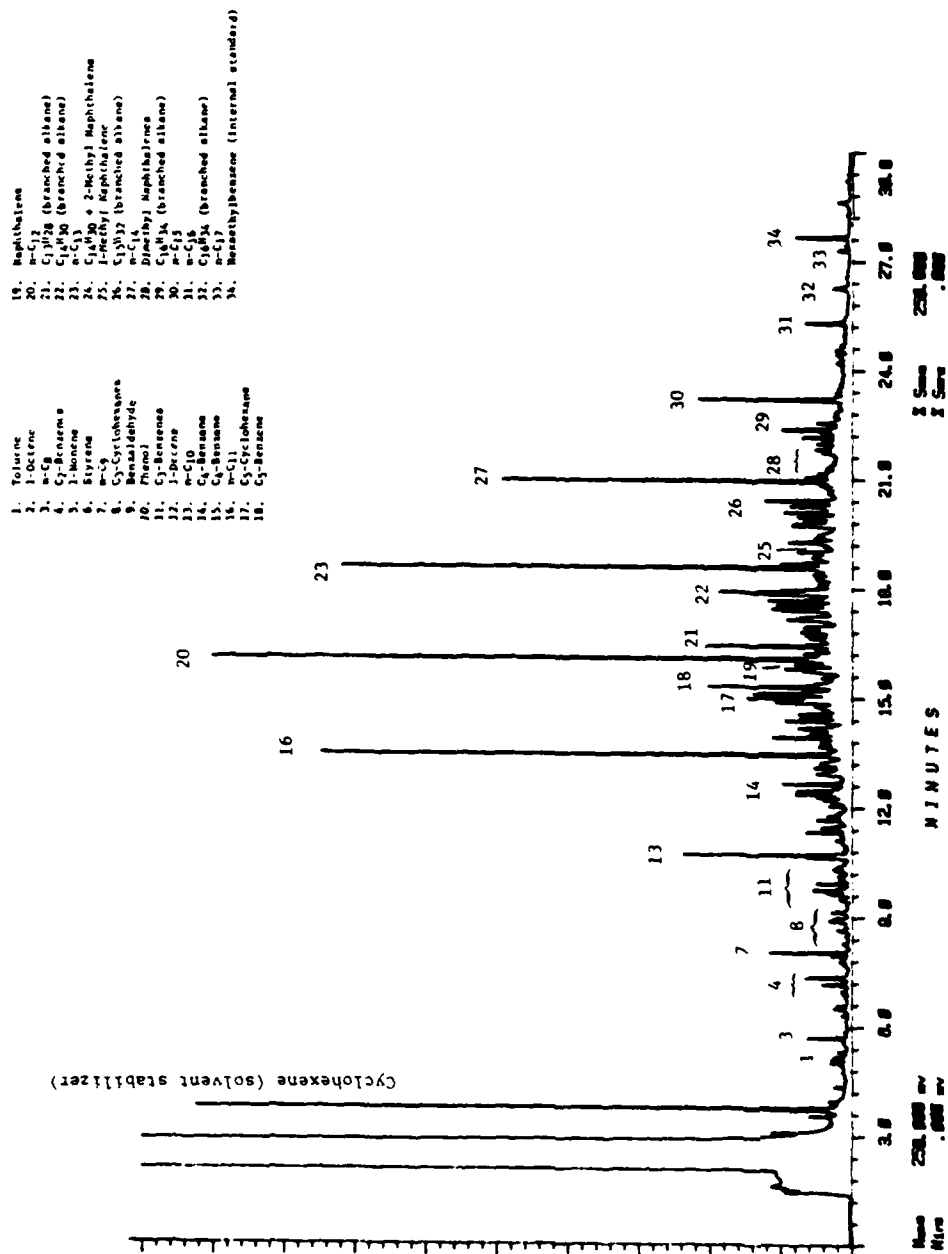


Figure 9. GC/FID Chromatogram of JP-5 Fuel Sample From Test 8

TABLE 12. PERCENT COMPOSITION IN JP-5 FUEL FROM COMBUSTOR RIG TESTS

Component	RT	6/23/82 Test			6/24/82 Test			6/30/82 Test			7/1/82 Test		
		#2	#3	#4	#6	#7	#8	#10	#11	#12	#14	#15	#16
n-C ₈	5.73	0.25	0.26	0.27	0.27	0.27	0.26	0.27	0.30	0.25	0.27	0.27	0.30
n-C ₉	8.08	0.58	0.63	0.54	0.64	0.64	0.61	0.62	0.63	0.64	0.61	0.60	0.68
n-C ₁₀	10.76	1.37	1.50	1.12	1.54	1.93	1.44	1.42	1.42	1.37	1.41	1.37	1.55
C ₁₀ -Benzene	12.70	0.65	0.66	0.40	0.65	0.64	0.60	0.58	0.56	0.56	0.57	0.56	0.66
C ₉ -Benzene	13.27	0.64	0.78	0.39	0.72	0.74	0.47	0.65	0.44	0.64	0.65	0.64	0.79
n-C ₁₁	13.51	4.85	5.38	3.53	5.63	5.41	5.10	5.01	5.03	4.92	5.20	4.76	5.58
C ₅ -Cyclohexane	15.08	1.02	1.20	0.70	1.10	1.15	1.05	1.11	1.08	1.03	1.10	1.14	1.22
C ₅ -Benzene	15.38	1.81	2.19	1.21	2.01	2.04	1.85	1.85	1.80	1.80	1.84	1.80	1.79
Naphthalene	15.97	0.61	0.71	0.40	0.67	0.68	0.63	0.63	0.62	0.60	0.62	0.60	0.76
n-C ₁₂	16.15	6.06	6.73	4.41	6.78	6.76	6.34	6.38	6.39	6.06	6.65	6.19	6.95
C ₁₃ H ₂₈ (branched alkane)	16.49	1.46	1.69	1.00	1.63	1.63	1.51	1.52	1.51	1.49	1.54	1.50	1.78
C ₁₄ H ₃₀ (branched alkane)	17.97	1.03	1.15	0.73	1.10	1.14	1.07	1.06	1.10	1.07	1.10	1.04	1.28
n-C ₁₃	18.65	4.78	5.64	3.70	5.58	5.59	5.24	5.32	5.33	5.23	5.28	5.19	6.07
1-Methyl Naphthalene	19.23	ND	ND	0.16	ND	ND	0.22	0.20	0.21	0.23	ND	ND	0.43
C ₁₅ H ₃₂ (branched alkane)	20.47	0.79	1.11	0.55	0.88	0.88	0.84	0.82	0.85	0.83	0.79	0.80	1.16
n-C ₁₄	21.02	3.02	3.47	2.31	3.35	3.37	3.16	3.20	3.26	3.18	3.20	3.12	3.78
C ₁₆ H ₃₄ (branched alkane)	22.41	0.66	0.92	0.42	0.76	0.75	0.67	0.70	0.72	0.70	0.70	0.68	0.47
n-C ₁₅	23.24	1.55	1.73	1.25	1.71	1.70	1.65	1.63	1.64	1.64	1.61	1.57	1.86
n-C ₁₆	25.35	0.37	0.41	0.42	0.41	0.40	0.40	0.41	0.43	0.40	0.38	0.36	0.44
C ₁₆ H ₃₄ (branched alkane)	26.32	0.11	0.14	0.18	0.08	0.09	0.19	0.15	0.15	0.15	0.14	0.10	0.20
C ₁₇	27.34	0.08	0.09	0.06	0.08	0.09	0.09	0.09	0.09	0.09	0.08	0.08	0.10
Total Identified Components (C ₁₀ -C ₁₇)		31	36	23	35	35	32	33	33	32	33	32	37
Total Resolved Components (C ₁₀ -C ₁₇)		66	82	46	74	75	70	68	69	66	69	70	86
Total (resolved + nonresolved) (C ₁₀ -C ₁₇)		88	97	65	91	93	96	85	85	84	87	85	94

- | | |
|---------------------------|------------------|
| 1. Ethane | 20. 1-Methane |
| 2. Ethylene | 21. 1-Methane |
| 3. Propane | 22. 1-Methane |
| 4. Acetylene | 23. 1-Methane |
| 5. Propene | 24. Toluene |
| 6. Acetaldehyde | 25. Methyl |
| 7. 1-Butene | 26. 1-Octene |
| 8. 1,3-Butadiene | 27. 1-Octene |
| 9. 1,3-Butadiene | 28. Ethylbenzene |
| 10. 2-Butene | 29. 1-Octene |
| 11. 2-Propenal (Acrolein) | 30. 1-Octene |
| 12. Acetone | 31. 1-Octene |
| 13. 1-Pentene | 32. 1-Octene |
| 14. 1-Pentene | 33. 1-Octene |
| 15. 1-Pentene | 34. Benzaldehyde |
| 16. 2-Methyl-2-Butene | 35. 1-Decene |
| 17. 1-Pentene | 36. 1-Decene |
| 18. 2-Methyl-2-Propenal | 37. Naphthalene |
| 19. 2-Methylpentene | |

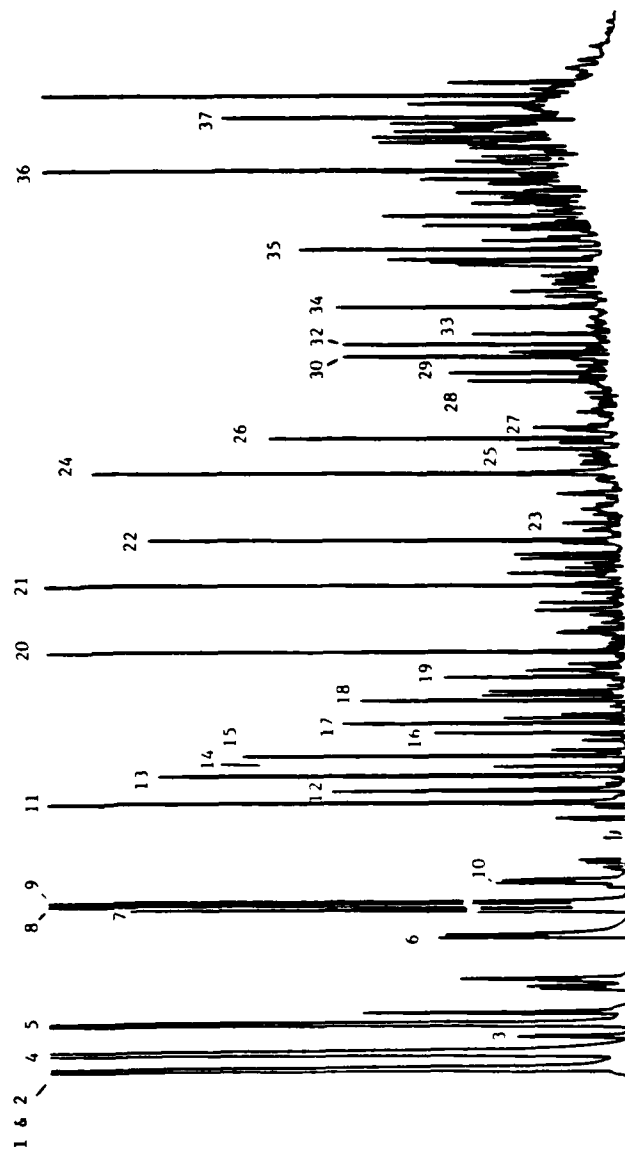


Figure 10. GC/FID Chromatogram of Combustor Rig Exhaust (Test 14) Using On-Line Cryogenic GC

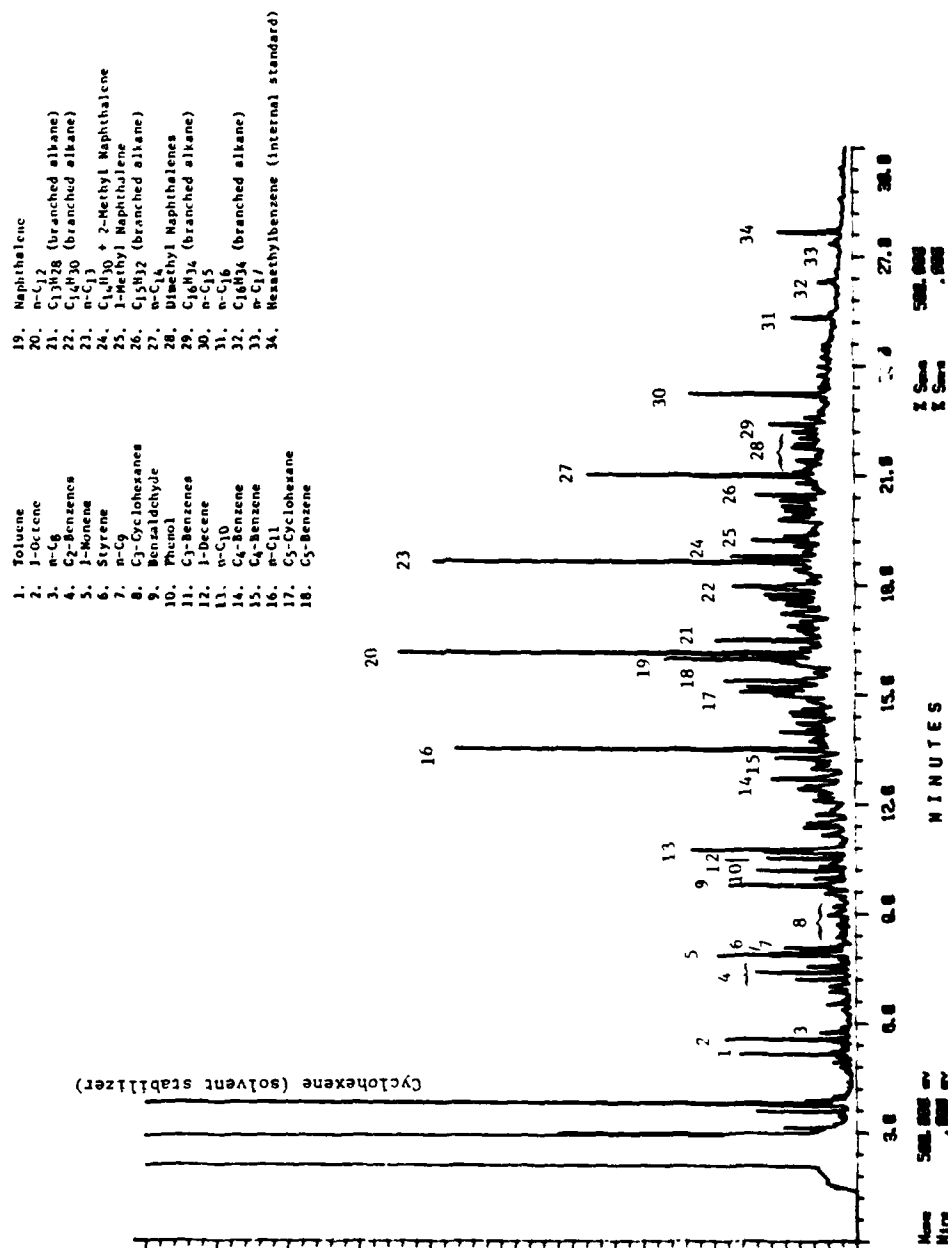


Figure 11. GC/FID Chromatogram of XAD Exhaust Sample from Test 8

17/23/20 7/12/1982
 Pol. Page 1

37504-76-02-AF0314-1
 1988.7 0.0 8 1988.7 8

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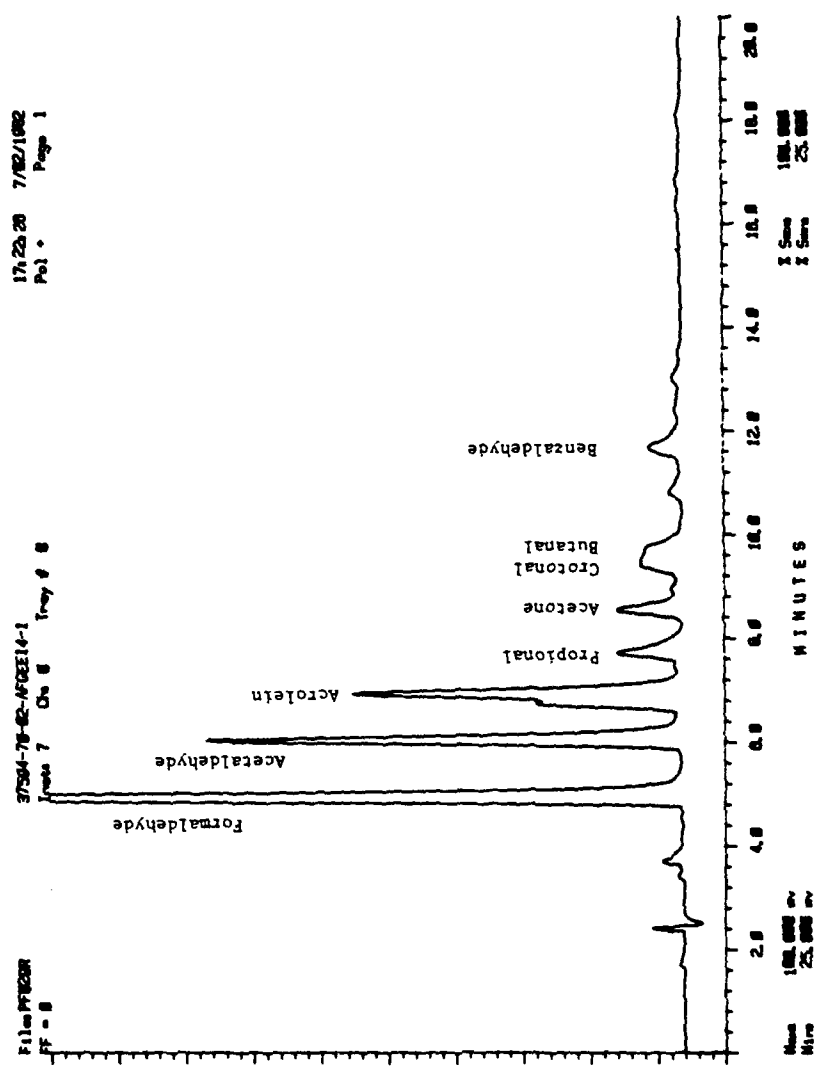


Figure 12. Chromatogram for DNPH/HPLC Analysis Test 14

TABLE 13. MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC
SAMPLING TECHNIQUE, COMBUSTOR RIG TESTS, 6/23/82

Compound [ppmC]	Test 2	Test 3	Test 4
1. Ethane	5.34	7.98	2.67
2. Ethylene	91.25	77.24	92.02
3. Propane	.37	.70	.73
4. Acetylene	25.18	21.04	23.72
5. Propene	33.04	28.33	31.80
6. Acetaldehyde	.91	3.56	6.18
7. 1-Butene	3.70	4.62	7.86
8. 1,3-Butadiene	9.27	2.22	13.03
9. C ₄ -ene	10.33	7.97	6.24
10. C-2-Butene	1.01	1.08	1.64
11. 2-Propenal (Acrolein)	8.32	7.98	8.65
12. Acetone	3.77	3.48	3.68
13. 1-Pentene	3.13	2.59	5.45
14. N-Pentane	.67	1.22	1.32
15. C ₅ -ene	3.87	3.78	3.82
16. 2-Methyl-2-Butene	1.41	1.30	.92
17. C ₅ -ene	1.82	1.73	.72
18. 2-Methyl-2-Propenal (or Crotonaldehyde)	1.57	1.36	2.26
19. 2-Methylpentane	1.47	1.38	1.49
20. 1-Hexene	5.53	5.09	5.42
21. Benzene	10.57	9.90	10.52
22. 1-Heptene	3.54	3.28	3.46
23. N-Heptane	.46	.45	.48
24. Toluene	3.74	3.61	3.81
25. Hexanal	1.15	1.09	1.19
26. 1-Octene	2.40	2.12	2.33
27. N-Octane	.26	.59	.32
28. Ethylbenzene	1.43	1.36	1.40
29. M+P-Xylene	1.92	1.98	2.02
30. Styrene	2.22	2.17	2.15
31. O-Xylene	1.08	1.10	1.07
32. 1-Nonene	2.12	2.09	2.04
33. N-Nonane	1.01	1.04	.93
34. Benzaldehyde	2.32	2.46	2.34
35. N-Decane	2.19	2.22	2.08
36. N-Undecane	7.25	7.90	7.15
37. Napthalene	3.74	4.17	3.45

TABLE 14. MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING
TECHNIQUE, COMBUSTOR RIG TESTS, 6/24/82

Compound [ppmC]	Test 6	Test 7	Test 8
1. Ethane	2.50	2.56	2.66
2. Ethylene	82.44	83.43	84.06
3. Propane	1.00	1.05	1.17
4. Acetylene	22.89	22.30	22.39
5. Propene	31.64	28.31	29.36
6. Acetaldehyde	.03	3.79	5.77
7. 1-Butene	3.31	8.22	4.80
8. 1,3-Butadiene	13.36	12.03	11.84
9. C ₄ -ene	10.98	6.00	9.37
10. C-2-Butene	.81	1.56	.93
11. 2-Propenal (Acrolein)	8.32	7.94	8.17
12. Acetone	3.82	3.56	3.81
13. 1-Pentene	5.50	5.22	5.20
14. N-Pentane	1.34	1.27	1.26
15. C ₅ -ene	4.03	3.96	3.90
16. 2-Methyl-2-Butene	1.22	1.37	1.11
17. C ₅ -ene	1.84	2.22	1.65
18. 2-Methyl-2-Propenal (or Crotonaldehyde)	2.50	2.19	2.29
19. 2-Methylpentane	1.52	1.44	1.56
20. 1-Hexene	5.48	5.22	5.14
21. Benzene	10.52	10.17	9.93
22. 1-Heptene	3.55	3.39	3.34
23. N-Heptane	.46	.48	.43
24. Toluene	3.85	3.66	3.61
25. Hexanal	1.33	1.15	1.14
26. 1-Octene	2.39	2.22	2.18
27. N-Octane	.82	.59	.60
28. Ethylbenzene	1.56	1.37	1.38
29. M+P-Xylene	2.04	1.84	2.01
30. Styrene	2.42	2.16	2.22
31. O-Xylene	1.31	1.06	1.16
32. 1-Nonene	2.34	1.97	2.10
33. N-Nonane	1.22	.96	1.05
34. Benzaldehyde	2.77	2.22	2.52
35. N-Decane	2.47	2.07	2.23
36. N-Undecane	8.95	7.09	8.20
37. Napthalene	4.80	3.71	4.31

TABLE 15. MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING
TECHNIQUE, COMBUSTOR RIG TESTS, 6/30/82

Compound [ppmC]	Test 10	Test 11	Test 12
1. Ethane	2.52	2.33	2.11
2. Ethylene	84.61	81.40	73.14
3. Propane	0.77	0.68	0.63
4. Acetylene	21.41	20.51	18.35
5. Propene	28.83	28.04	25.00
6. Acetaldehyde	5.41	5.16	5.07
7. 1-Butene	8.68	3.74	3.09
8. 1,3-Butadiene	10.74	10.44	10.11
9. C ₄ -ene	3.60	8.02	8.15
10. C-2-Butene	1.63	0.84	0.70
11. 2-Propenal (Acrolein)	7.10	7.17	6.79
12. Acetone	2.64	3.10	3.06
13. 1-Pentene	4.63	4.52	4.35
14. N-Pentane	0.10	1.05	1.03
15. C ₅ -ene	3.33	2.81	2.95
16. 2-Methyl-2-Butene	1.13	0.75	0.97
17. C ₅ -ene	2.39	1.02	1.76
18. 2-Methyl-2-Propenal (or Crotonaldehyde)	2.23	2.38	2.15
19. 2-Methylpentane	1.32	1.26	1.24
20. 1-Hexene	4.58	4.45	4.26
21. Benzene	8.72	8.44	8.02
22. 1-Heptene	2.93	2.90	2.78
23. N-Heptane	0.40	0.44	0.45
24. Toluene	3.14	3.02	2.39
25. Hexanal	1.05	0.54	0.93
26. 1-Octene	1.97	1.89	1.81
27. N-Octane	0.56	0.49	0.47
28. Ethylbenzene	1.21	1.17	1.10
29. M+P-Xylene	1.56	1.53	1.45
30. Styrene	1.89	1.85	1.79
31. O-Xylene	0.94	0.97	0.93
32. 1-Nonene	1.75	1.82	1.74
33. N-Nonane	0.88	0.90	0.89
34. Benzaldehyde	1.95	2.13	2.02
35. N-Decane	1.70	1.95	1.87
36. N-Undecane	5.83	6.92	6.69
37. Napthalene	2.94	2.91	3.12

TABLE 16. MAJOR SPECIES QUANTIFIED BY THE CRYOGENIC SAMPLING
TECHNIQUE, COMBUSTOR RJG TESTS, 7/1/82

Compound (ppmC)	Test 14	Test 15	Test 16
1. Ethane	2.21	2.38	2.37
2. Ethylene	77.80	80.01	82.41
3. Propane	0.75	1.68	0.71
4. Acetylene	18.61	20.02	20.27
5. Propene	26.52	27.76	28.40
6. Acetaldehyde	1.83	5.17	5.16
7. 1-Butene	5.83	10.72	10.38
8. 1,3-Butadiene	11.13	12.60	11.74
9. C ₄ -ene	7.60	*	*
10. C-2-Butene	1.31	2.35	2.10
11. 2-Propenal (Acrolein)	7.42	7.34	6.88
12. Acetone	3.43	1.88	3.01
13. 1-Pentene	5.01	4.28	4.10
14. N-Pentane	1.18	1.11	1.04
15. C ₅ -ene	3.14	3.08	3.02
16. 2-Methyl-2-Butene	1.26	1.02	0.80
17. C ₅ -ene	1.94	1.95	1.79
18. 2-Methyl-2-Propenal (or Crotonaldehyde)	2.79	2.47	2.09
19. 2-Methylpentane	1.35	1.29	1.24
20. 1-Hexene	4.98	4.67	4.47
21. Benzene	9.07	8.61	8.23
22. 1-Heptene	3.16	3.14	2.87
23. N-Heptane	0.44	0.42	0.40
24. Toluene	3.33	3.10	3.00
25. Hexanal	1.09	1.04	0.98
26. 1-Octene	2.13	1.99	1.91
27. N-Octane	0.63	0.55	0.54
28. Ethylbenzene	1.33	1.17	1.13
29. M+P-Xylene	1.70	1.53	1.49
30. Styrene	2.01	1.82	1.77
31. O-Xylene	1.06	0.95	0.93
32. 1-Nonene	1.91	1.75	1.71
33. N-Nonane	0.99	0.83	0.82
34. Benzaldehyde	2.12	1.94	1.89
35. N-Decane	2.00	1.82	1.71
36. N-Undecane	8.05	6.81	5.81
37. Napthalene	3.52	1.74	2.21

* Compound not resolved from peaks 7 and 8.

TABLE 17. MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING
TECHNIQUE, COMBUSTION RIG TESTS, 6/23/82

Compound	RT, Minutes	Concentration (ppmC)		
		Test 2	Test 3	Test 4
1. n-C ₉	8.08	1.57	1.58	1.54
2. Benzaldehyde	9.78	1.49	1.57	1.52
3. Phenol	10.19	0.88	1.04	1.07
4. 1-Decene	10.53	1.02	0.97	0.97
5. n-C ₁₀	10.76	2.10	2.05	2.01
6. C ₄ -Benzene	12.70	1.60	1.53	1.51
7. C ₄ -Benzene	13.27	1.55	1.11	1.18
8. n-C ₁₁	13.51	6.42	6.05	5.75
9. C ₅ -Cyclohexane	15.08	1.67	1.59	1.56
10. C ₅ -Benzene	15.38	2.00	1.91	1.78
11. Naphthalene	15.97	2.88	2.73	2.62
12. n-C ₁₂	16.15	7.78	7.23	7.35
13. C ₁₃ H ₂₈ (Branched Alkane)	16.49	2.01	1.85	1.84
14. C ₁₄ H ₃₀ (Branched Alkane)	17.97	1.56	1.44	1.34
15. n-C ₁₃	18.65	6.97	6.27	6.11
16. 1-Methyl Naphthalene	19.23	1.04	0.95	0.93
17. C ₁₅ H ₃₂ (Branched Alkane)	20.47	1.22	1.21	1.08
18. n-C ₁₄	21.02	4.37	4.26	3.91
19. C ₁₆ H ₃₄ (Branched Alkane)	22.41	0.90	0.81	0.88
20. n-C ₁₅	23.24	2.45	2.32	2.38
21. n-C ₁₆	25.35	0.69	0.60	0.60
22. C ₁₆ H ₃₄ (Branched Alkane)	26.32	0.55	0.40	0.35
23. n-C ₁₇	27.34	0.12	0.14	0.11

TABLE 18. MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING
TECHNIQUE, COMBUSTION RIG TESTS, 6/24/82

Compound	RT, Minutes	Concentration (ppmC)		
		Test 6	Test 7	Test 8
1. n-C ₉	8.08	1.61	1.08	1.47
2. Benzaldehyde	9.78	1.58	1.10	1.45
3. Phenol	10.19	0.94	0.70	1.02
4. 1-Decene	10.53	1.03	0.70	0.92
5. n-C ₁₀	10.76	2.16	1.64	1.89
6. C ₁₀ -Benzene	12.70	1.57	1.07	1.46
7. C ₁₁ -Benzene	13.27	1.24	0.83	1.37
8. n-C ₁₁	13.51	6.36	4.30	5.68
9. C ₅ -Cyclohexane	15.08	1.59	1.21	1.50
10. C ₅ -Benzene	15.38	2.00	1.22	1.77
11. Naphthalene	15.97	2.85	1.94	2.62
12. n-C ₁₂	16.15	7.58	5.42	6.80
13. C ₁₃ H ₂₈ (Branched Alkane)	16.49	1.97	1.31	1.79
14. C ₁₄ H ₃₀ (Branched Alkane)	17.97	1.47	0.92	1.38
15. n-C ₁₃	18.65	6.70	4.34	5.93
16. 1-Methyl Naphthalene	19.23	0.98	0.64	0.89
17. C ₁₅ H ₃₂ (Branched Alkane)	20.47	1.21	0.82	1.12
18. n-C ₁₄	21.02	4.28	3.03	4.28
19. C ₁₆ H ₃₄ (Branched Alkane)	22.41	0.84	0.64	6.81
20. n-C ₁₅	23.24	2.42	1.67	2.28
21. n-C ₁₆	25.35	0.60	0.41	0.57
22. C ₁₆ H ₃₄ (Branched Alkane)	26.32	0.26	0.20	0.33
23. n-C ₁₇	27.34	0.12	0.09	0.15

TABLE 19. MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING
TECHNIQUE, COMBUSTION RIG TESTS, 6/30/82

Compound	RT, Minutes	Concentration (ppmC)		
		Test 10	Test 11	Test 12
1. n-C ₉	8.08	1.20	1.15	1.19
2. Benzaldehyde	9.78	1.18	1.18	1.22
3. Phenol	10.19	0.83	0.85	0.86
4. 1-Decene	10.53	0.80	0.77	0.80
5. n-C ₁₀	10.76	1.64	1.78	1.66
6. C ₄ -Benzene	12.70	1.25	0.95	0.97
7. C ₄ -Benzene	13.27	0.95	1.14	1.05
8. n-C ₁₁	13.51	4.78	4.64	4.78
9. C ₅ -Cyclohexane	15.08	1.28	1.22	1.35
10. C ₅ -Benzene	15.38	1.51	1.44	1.55
11. Naphthalene	15.97	2.15	2.07	2.15
12. n-C ₁₂	16.15	5.80	5.98	6.23
13. C ₁₃ H ₂₈ (Branched Alkane)	16.49	1.53	1.48	1.61
14. C ₁₄ H ₃₀ (Branched Alkane)	17.97	1.08	1.11	1.19
15. n-C ₁₃	18.65	4.89	4.96	5.32
16. 1-Methyl Naphthalene	19.23	0.62	0.68	0.76
17. C ₁₅ H ₃₂ (Branched Alkane)	20.47	0.93	0.89	0.95
18. n-C ₁₄	21.02	3.41	3.26	3.51
19. C ₁₆ H ₃₄ (Branched Alkane)	22.41	0.70	0.65	0.70
20. n-C ₁₅	23.24	1.96	1.79	1.92
21. n-C ₁₆	25.35	0.65	0.66	0.61
22. C ₁₆ H ₃₄ (Branched Alkane)	26.32	0.14	0.31	0.19
23. n-C ₁₇	27.34	0.11	0.09	0.09

TABLE 20. MAJOR SPECIES QUANTIFIED BY THE XAD SAMPLING
TECHNIQUE, COMBUSTION RIG TESTS, 7/1/82

Compound	RT, Minutes	Concentration (ppmC)		
		Test 14	Test 15	Test 16
1. n-C ₉	8.08	1.32	1.24	1.20
2. Benzaldehyde	9.78	1.33	1.24	1.22
3. Phenol	10.19	0.90	0.86	0.87
4. 1-Decene	10.53	0.89	0.85	0.83
5. n-C ₁₀	10.76	1.89	1.78	1.87
6. C ₄ -Benzene	12.70	1.41	1.33	0.99
7. C ₄ -Benzene	13.27	1.09	1.28	1.22
8. n-C ₁₁	13.51	5.52	5.14	4.89
9. C ₅ -Cyclohexane	15.08	1.48	1.38	1.33
10. C ₅ -Benzene	15.38	1.77	1.63	1.45
11. Naphthalene	15.97	2.35	2.25	2.04
12. n-C ₁₂	16.15	6.90	6.81	5.98
13. C ₁₃ H ₂₈ (Branched Alkane)	16.49	1.77	1.70	1.58
14. C ₁₄ H ₃₀ (Branched Alkane)	17.97	1.26	1.39	1.14
15. n-C ₁₃	18.65	5.80	5.45	5.32
16. 1-Methyl Naphthalene	19.23	0.80	0.81	0.70
17. C ₁₅ H ₃₂ (Branched Alkane)	20.47	1.10	1.04	0.96
18. n-C ₁₄	21.02	3.95	3.76	3.77
19. C ₁₆ H ₃₄ (Branched Alkane)	22.41	0.78	0.77	0.70
20. n-C ₁₅	23.24	2.18	2.14	1.93
21. n-C ₁₆	25.35	0.70	0.74	0.51
22. C ₁₆ H ₃₄ (Branched Alkane)	26.32	0.20	0.18	0.20
23. n-C ₁₇	27.34	0.11	0.11	0.10

TABLE 21. ALDEHYDUS QUANTIFIED BY THE DNPH/HPLC TECHNIQUE

Concentration (ppmC)						
	Formaldehyde	Acetaldehyde	Acrolein	Propional	Croton- aldehyde	Benz- aldehyde
<u>6/23/82</u>						
Test 1 (background air)	0.027(0.007) *	0.02(0.004)	0.018(0.006)	0.018(0.01)	ND	0.028(0.007)
Test 2**	6.66(0.56)	3.56(0.47)	3.54(1.26)	0.96(0.24)	1.6(0.48)	0.98(0.14)
Test 3	16.7(1.7)	6.46(0.61)	6.54(1.56)	1.92(0.30)	2.86(0.39)	2.52(0.21)
Test 4	13.8(0.71)	6.62(0.80)	6.45(1.2)	1.95(0.21)	1.57(0.30)	2.17(0.14)
<u>6/24/82</u>						
Test 5 (background air)	0.024	0.039	0.027	0.024	0.024	0.056
Test 6	16.1	8.06	7.35	2.37	1.88	2.52
Test 7	12.7	6.42	6.90	1.95	2.96	1.96
Test 8	13.8	5.46	7.11	1.83	2.72	2.03
<u>6/30/82</u>						
Test 9 (background air)	0.054	0.046	ND	ND	ND	ND
Test 10	11.3	4.68	5.61	1.44	1.04	0.77
Test 11	10.6	4.68	.23	1.32	0.92	0.70
Test 12	8.1	2.86	3.75	0.90	ND	ND
<u>7/1/82</u>						
Test 14**	10.2(ND)	7.26(0.19)	7.38(0.48)	2.10(ND)	2.60(ND)	1.40 (ND)
Test 15	30.0	16.9	14.6	4.53	7.12	6.86
Test 16	12.4	7.58	6.75	2.10	2.80	1.19

* Concentration in second impinger given in parenthesis for samples where impingers were analyzed separately.

** These two data sets (Tests 2 and 15) appear to be outliers.

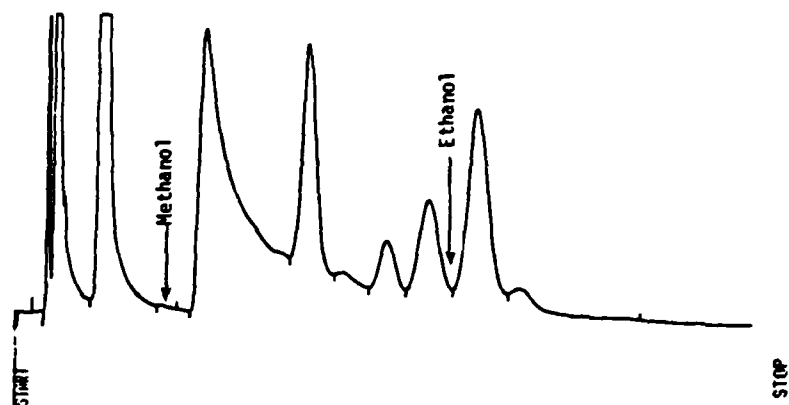


Figure 13. Chromatogram of Bag Sample Collected During Test 11

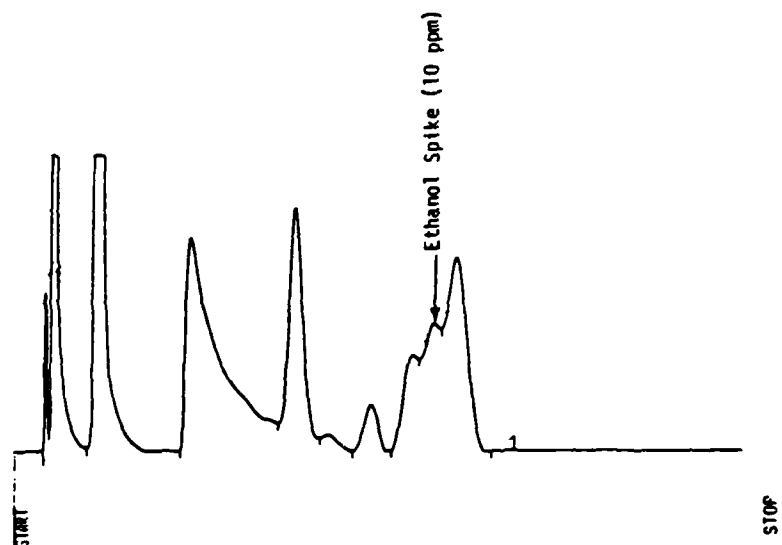


Figure 14. Chromatogram of Bag Sample Collected During Test 11 After Spiking With 10 ppm Ethanol

TABLE 22. PNA CONCENTRATIONS IN SELECTED XAD AND FUEL SAMPLES, $\mu\text{g}/\text{m}^3$

Compound	MW	Test 3	Test 11	Test 14	Test 15(a)	Test 10(a)	Test 5(b)	Test 9(b)	Test 14(c) Backup	Test 15(c) Backup	JP-5 Fuel #3(d)
Naphthalene	128	S ^(e)	S	S	S	S	4.0	4.1	1.2	0.97	S
2-Methyl Naphthalene	142	S	S	S	S	S	1.5	1.2	0.29	0.10	820
1-Methyl Naphthalene	142	S	S	S	S	S	0.80	0.67	0.11	0.06	560
Dimethylnaphthalene (isomer)	156	250	140	130	95	170	0.26	0.27	0.04	ND ^(f)	700
Dimethylnaphthalene ((isomer))	156	360	210	160	200	250	0.44	0.49	0.08	ND	980
Dimethylnaphthalene (isomer)	156	140	68	65	72	87	0.14	0.14	0.03	ND	240
Dimethylnaphthalene (isomer)	156	60	22	19	23	23	0.05	0.05	0.01	ND	76
Phenanthrene	178	40	26	27	23	27	1.8	1.1	0.25	0.15	4.8
Anthracene	178	7.3	3.4	4.2	21	22	ND	ND	ND	ND	ND
Fluoranthene	202	17	11	12	11	12	0.22	0.22	0.11	0.08	ND
Pyrene	202	9.8	7.5	8.0	7.4	(No data)	0.21	0.13	0.09	0.11	ND
Benzo(a)anthracene	228	0.70	0.93	0.73	1.2	0.61	0.04	ND	ND	ND	ND
Chrysene	228	1.2	1.5	1.3	23	25	0.07	ND	ND	0.28	ND
Benzo(c)pyrene	252	1.2	0.60	0.80	26	28	0.09	ND	ND	0.54	ND
Benzo(a)pyrene	252	0.97	0.60	0.72	23	26	0.10	ND	ND	ND	ND
Perylene	252	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

(a) These samples were spiked with $20 \mu\text{g}/\text{m}^3$ of anthracene, chrysene, benzo(c)pyrene, and benzo(a)pyrene prior to sampling.

(b) These tests (5 and 9) were background air samples.

(c) XAD cartridge placed behind primary cartridge during sampling to check for breakthrough.

(d) Fuel concentrations given in units of $\mu\text{g}/\text{g}$.

(e) Peak saturated.

(f) ND = Not detected. Detection limit approximately $0.05 \mu\text{g}/\text{m}^3$ in exhaust and $0.1 \mu\text{g}/\text{g}$ in fuel.

appropriate for subsequent interpretation, because the latter monitor sampled precisely the same gas stream as our array of analytical methods for organic speciation. The recorder trace from this FID monitor is reproduced in Figure 15-18 for all 12 combustor rig exhaust experiments.

Since the individual fuel samples collected for each test were virtually identical when analyzed by capillary GC, a composite sample was subjected to the standard fuel analysis procedures. Results of these tests are shown in Table 23, along with the appropriate specification values. The composite fuel sample met or exceeded all specifications for JP-5 with the exception of flash point which was 53°C versus a specified minimum value of 60°C. The lower flash point is a result of the presence of a trace amount of volatile material (<<10 percent as evidenced by the initial boiling point data) and is expected to have no detectable effect on the character of organic emissions from the combustor.

The particle (filter) and gaseous phase (XAD-2) samples collected for bioassay were subjected to a preliminary Ames Salmonella mutagenesis assay. Mutagenic activity was observed for both samples, although the total mutagenic activity in the XAD-2 extract was 20 times greater than for the filter sample. Virtually all of the mutagenic activity in the samples was direct-acting (did not require metabolic activation). GC/MS analyses of the filter extract failed to detect significant levels of any components other than phthalate esters (plasticizers) which were presumably present as contaminants. The direct-acting mutagens, nitro PAHs, were not detected in either the filter or XAD-2 samples.

The environmental significance of the observed mutagenicity cannot be determined from the limited data obtained in this study. However, similar levels of mutagenicity have been observed for diesel particle extracts. In addition, virtually all combustion sources, as well as ambient particulate matter, exhibit some mutagenic activity (10,11). Further bioassay studies of the turbine emissions would be required to determine the relative impact compared to other emission sources.

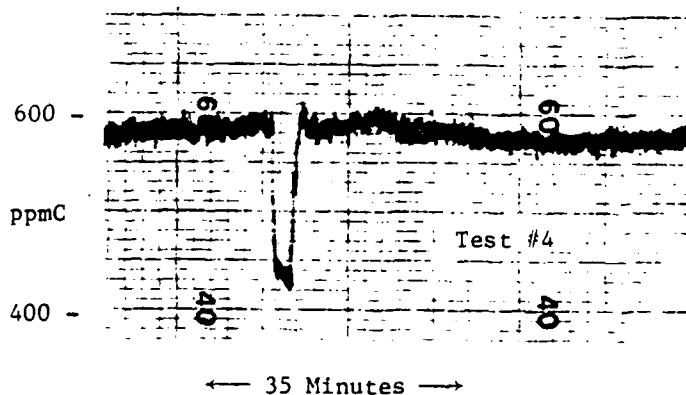
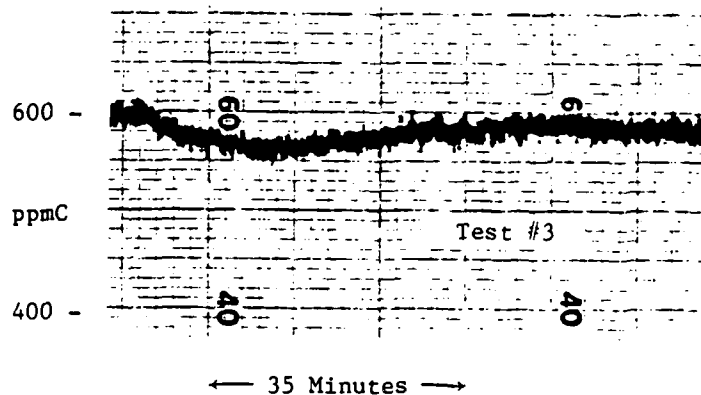
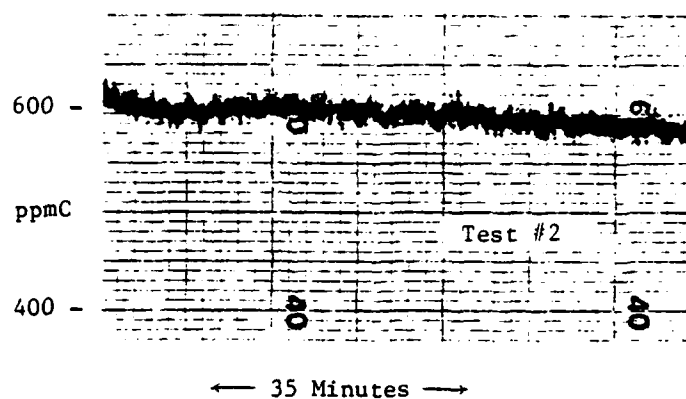
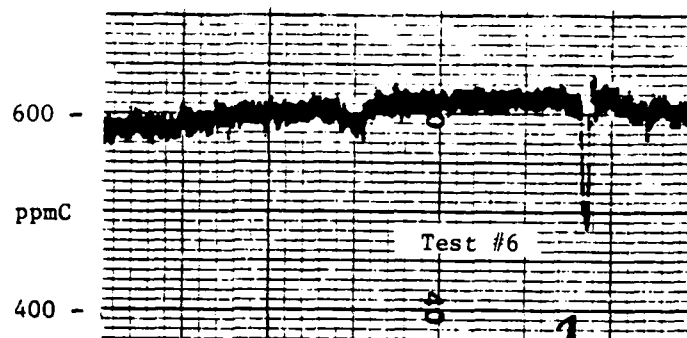
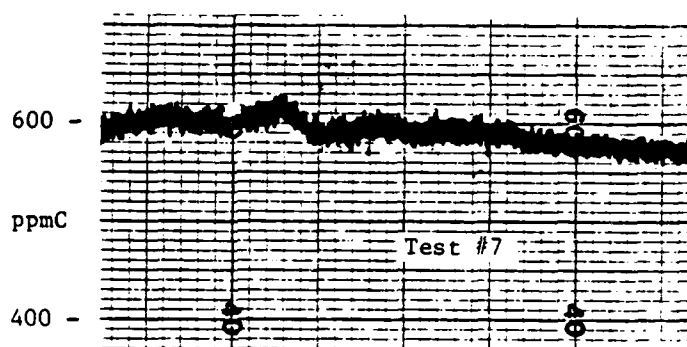


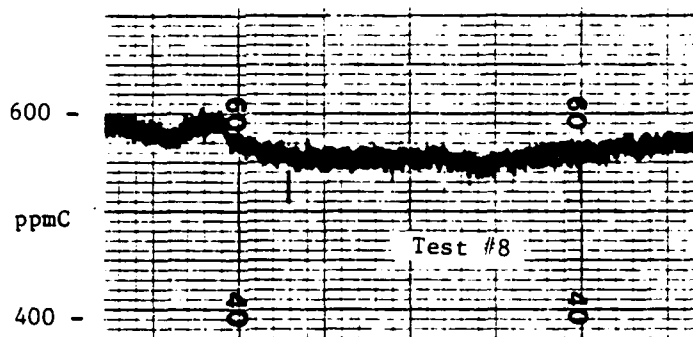
Figure 15. Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 2, 3 and 4



← 35 Minutes →



← 35 Minutes →



← 35 Minutes →

Figure 16. Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 6, 7 and 8

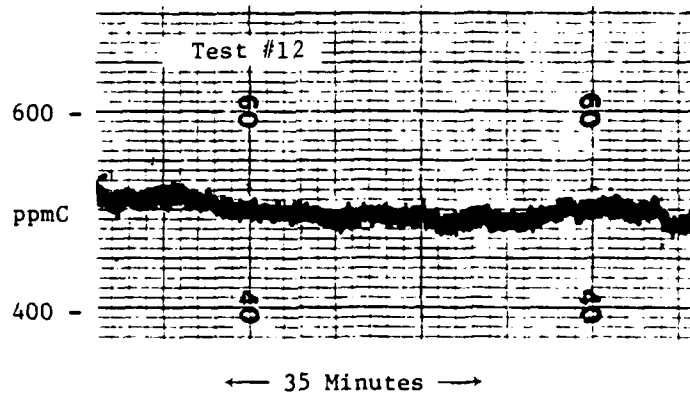
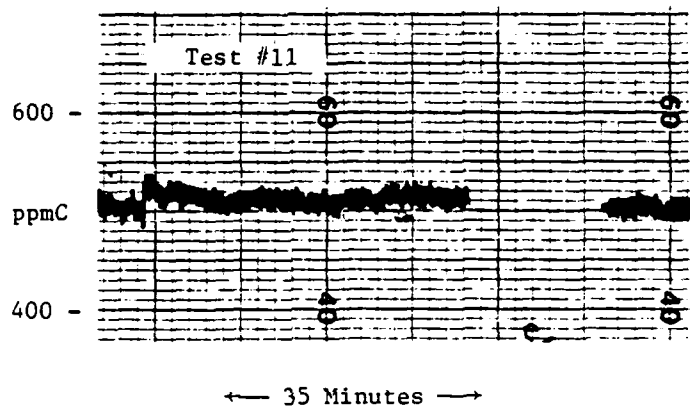
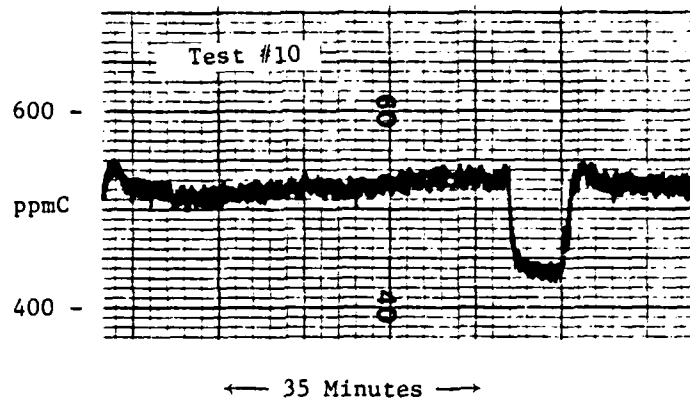
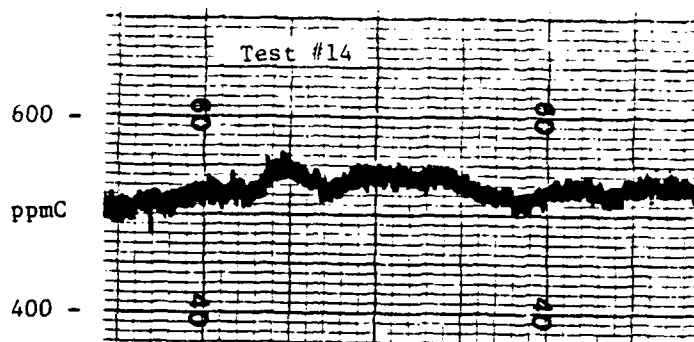
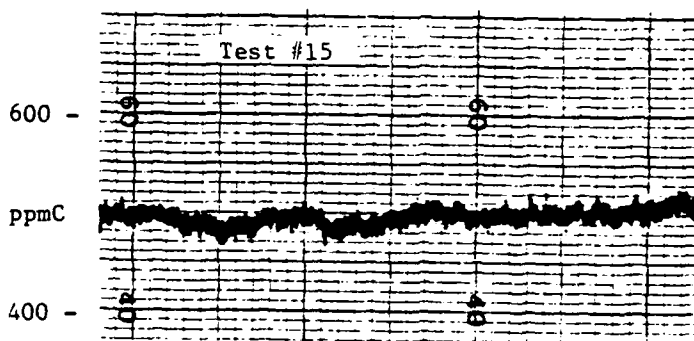


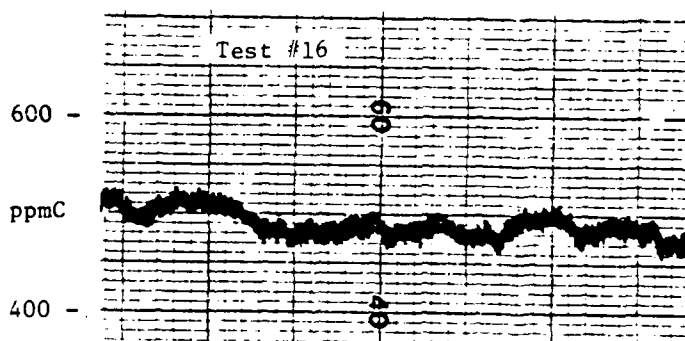
Figure 17. Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 10, 11 and 12



← 35 Minutes →



← 35 Minutes →



← 35 Minutes →

Figure 18. Continuous FID Response (Beckman 402) From Manifold During Combustor Rig Tests 14, 15 and 16

TABLE 23. STANDARD FUELS ANALYSIS DATA

Test Parameter	ASTM Method	Value for Test Fuel	Specification (a)
Color, Saybolt	D156	26	--
Total acid number, mg KOH/g	D3242	0.002	0.015 (max)
Gravity, ° API	D1298	43.5	36-48
Copper strip corrosion	D130	1a	1b (max)
Existent gum, MG/100 mL	D381	0.0	7.0 (max)
Viscosity at 20 °C, CS	D445	6.0	8.5 (max)
Particulate, mg/L	D2276	0.1	1.0 (max)
Aromatics, vol %	D1319	17.9	25 (max)
Olefins, vol %	D1319	1.6	5 (max)
Mercaptan sulfur, wt %	D3227	0.000	0.001 (max)
Total sulfur, wt %	D2622	0.00	0.40 (max)
Luminometer number	D1740	55	--
Smoke Point, mm	D1322	21	19 (min)
FSII, vol %	H5327	0.13	--
WSIM	D3948	79	--
Flash point, °C	D93	53	60 (min)
Freezing point, °C	D2386	-43	-46 (max)
Net heat of combustion, MJ/KG	D3338	43.3	42.6 (min)
Hydrogen content, wt %	D3343	13.8	13.5 (min)
Simulated distillation	D2887		--
Initial boiling point		58 °C	
10%		159 °C	
20%		184 °C	
50%		218 °C	
90%		264 °C	
End point		312 °C	
Distillation	D87		--
Initial boiling point		169 °C	
10%		185 °C	
20%		204 °C	
50%		219 °C	
90%		247 °C	
End point		268 °C	
Residue		1%	
Loss		1%	

(a) Mil-T-5624L, May 18, 1979.

C. DISCUSSION

1. Overview

The suitability of the sampling and analysis systems and procedures developed in Task 1 has been demonstrated through the Task 2 data presented in the previous section. Each of the sampling and analysis systems gave data with equivalent or superior reproducibility to that obtained in Task 1. The important aspects of the data to be discussed separately below include (1) the distribution (volatility and functionality) of organic species identified in the combustor rig exhaust, (2) the carbon balance obtained by comparing the total hydrocarbon value from FID to the summation of organic components detected in the exhaust sample, and (3) the performance characteristics of the various sampling and analysis systems.

2. Distribution of Organic Components in Combustor Rig Exhaust

An overview of the organic species detected in the exhaust during each test is given in Table 24. The background air (Tests 1, 5, and 9) contained negligible quantities of organics, with methane accounting for over half of the total hydrocarbons.

The total hydrocarbon concentrations (FID) found in the test runs varied between 490 and 600 ppmC, with good agreement between the total hydrocarbons by FID and the summation of organics detected by the sampling and analysis system. A detailed evaluation of this carbon balance aspect of the data is given in the following section.

Approximately 65 percent of the total hydrocarbon concentration was accounted for by components more volatile than normal decane ($n\text{-C}_{10}$). Detailed breakdowns of the volatility and functional group distribution of organics for a typical run (Test 14) are given in Tables 24, 25, and 26. Individual compounds identified in the exhaust are summarized in Tables 13-16 and Figures 10-12. Major volatile species identified include ethylene (80 ppmC), acetylene (20 ppmC), propene (27 ppmC), and 1,3-butadiene (12 ppmC). The vast majority of compounds identified with volatility greater than $n\text{-C}_{10}$ were olefins, aldehydes, or aromatics with minor quantities of aliphatics detected. This compound distribution, coupled with the high NO_2/NO_x ratio (Table 11), forms a highly reactive exhaust mixture, from a

TABLE 24. SUMMARY OF ORGANIC SPECIES MEASURED BY VARIOUS SAMPLING AND ANALYSIS METHODS, ppmC

	6/23/82				6/24/82				6/30/82				7/1/82			
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#14	#15	#16	Test
C ₄ (G.C.-F.I.D.)	1.9	11.4	11.6	11.3	2.1	12.1	11.4	11.4	1.9	10.1	9.3	9.3	9.6	9.5	9.2	
C ₂ through C ₉ (Cryogenic) (a)	0.2	334	319	327	1.3	347	325	324	.7	282	270	263	285	279	268	
C ₁₀ through C ₁₇ (XAD-2)	<1.0	182	185	170	<1.0	179	126	172	<1.0	146	136	144	165	151	146	
PAH (3+ rings) (b)	<0.001										<0.01		<0.01			
Aldehydes (DNPH)	0.15	20.5	41.8	35.9	0.19	38.3	32.9	33.0	0.10	24.8	22.5	23.7	31.6	80.0	32.8	
Total Organics by Species Summation	3.3	548	557	544	4.6	576	495	540	3.7	463	438	440	491	520	456	
Total Organics by Continuous F.I.D. Method	3.2	600	585	580	5.0	600	595	570	4.6	515	510	500	525	495	490	
Total Organics by Method 25(c)	-	-	-	-	-	-	-	-	12.6	451	367	231	190/217	619	423	

(a) Cryogenic data excludes aldehyde species.

(b) PAH analyses were completed for select tests.

(c) PEDCO indicated that samples for Tests 1-8 were contaminated during analysis.

TABLE 25. TOTAL ORGANIC SPECIES CONTRIBUTION BY CARBON NUMBER

Compound	ppmC
C ₁ to C ₂	19.8
C ₂ to C ₃	124.7
C ₃ to C ₄	44.9
C ₄ to C ₅	47.4
C ₅ to C ₆	24.7
C ₆ to C ₇	22.2
C ₇ to C ₈	14.2
C ₈ to C ₉	14.4
C ₉ to C ₁₀	13.7
C ₁₀ to C ₁₁	16.3
C ₁₁ to C ₁₂	33.6
C ₁₂ to C ₁₃	35.9
C ₁₃ to C ₁₄	33.6
C ₁₄ to C ₁₅	22.7
C ₁₅ to C ₁₆	12.6
C ₁₆ to C ₁₇	7.1
C ₁₇ and above	2.9
Total Organics	490.7

TABLE 26. MAJOR IDENTIFIED COMPOUNDS FROM TEST #14 GROUPED INTO THE FOLLOWING CLASSES

Compound	ppmC
Paraffins	41.2
Acetylene	18.6
Olefins	155.0
Aromatics	25.9
Aldehydes	31.6
Ketones	3.4
Alcohols	0.9
Total Identified Organics	276.6

photochemical standpoint. Comparison of these combustor rig data to those obtained from actual engine operation (Task 3) will be extremely interesting and of considerable significance in the evaluation of environmental effects from jet engine emissions.

Compounds with volatility less than $n\text{-C}_{10}$ were largely characteristic of the JP-5 fuel. Comparison of Figures 9 and 10 reveals the similarity between the JP-5 fuel and XAD sample extract. However, several important differences are discussed later in this section.

The major components less volatile than $n\text{-C}_{10}$ were normal alkanes ($n\text{-C}_{10}$ to $n\text{-C}_{17}$), branched alkanes, cycloalkanes, and alkyl benzenes. Virtually no olefinic material was detected in either the fuel or the XAD extract. As shown in Figures 9 and 11, both the XAD extract and fuel were extremely complex and only a portion of the total hydrocarbon content was identified (~40 percent). A substantial portion (~30 percent) was represented by a broad unresolved envelope characteristic of petroleum distillates. Although this unresolved envelope was readily quantified by fused silica capillary GC/FID, identification of the vast number of components comprising the envelope was impractical.

Identification and quantification of all the resolved components in the XAD extract and fuel were also impractical, although most of the major components were identified (Tables 12 and 17-20). Because of differences in relative response and other factors between GC/MS and GC/FID, not all of the components identified by GC/MS could be correlated with a specific peak in the GC/FID trace. Consequently, semiquantitative data from the GC/MS analysis of a typical XAD and fuel sample are presented in Table 27 to more thoroughly describe the organic content of these samples. As shown in Table 27, a wide variety of alkylbenzenes, alkylcyclohexanes, and aliphatics was detected, whereas no olefins were detected.

Careful comparison of the XAD and fuel data in Table 27 and Figures 9 and 11 reveals a relative increase of naphthalene and alkyl-naphthalenes in the XAD extract compared to the fuel sample. A more graphic illustration of this aspect of the data is presented in Table 28, wherein volatilities are presented. As shown in Table 28, the aromatic/aliphatic ratio for the XAD sample is substantially greater in all cases. This

TABLE 27. GC/MS IDENTIFICATION OF EXHAUST AND FUEL COMPONENTS

Component ^(a)	Relative Concentration (n-C ₁₂ = 1.00)	
	XAD Test #15	Fuel Test #15
Toluene	0.15	0.03
1-Octene	0.15	ND
n-C ₈	0.03	0.15
C ₂ -Cyclohexane	ND	0.03
C ₉ H ₂₀ (branched alkane)	ND	0.03
C ₉ H ₂₀ (branched alkane)	ND	0.03
C ₂ -Cyclohexane	ND	0.03
C ₃ -Cyclohexane	ND	0.03
C ₉ H ₂₀ (branched alkane)	0.01	0.03
C ₉ H ₂₀ (branched alkane)	0.01	0.03
C ₂ -Benzene	0.04	ND
C ₂ -Benzene	0.15	0.10
Nonene	0.15	ND
Syrene	0.20	ND
n-C ₉	0.05	0.35
C ₃ -Cyclohexane	ND	0.02
C ₃ -Cyclohexane	ND	0.03
C ₃ -Cyclohexane	ND	0.05
Benzaldehyde	0.20	ND
Phenol	0.05	ND
Decene	0.15	ND
n-C ₁₀	0.20	0.40
C ₃ -Benzene	0.20	0.05
C ₁₁ H ₂₄ (branched alkane)	0.10	0.10
C ₃ -Benzene	0.10	0.10
C ₄ -Cyclohexane	0.05	0.10
C ₄ -Benzene	0.15	0.15
Alkane	0.05	0.15
Alkane	0.05	0.15

TABLE 27. GC/MS IDENTIFICATION OF EXHAUST AND FUEL COMPONENTS (Continued)

Component (a)	Relative Concentration (n-C ₁₂ = 1.00)	
	XAD Test #15	Fuel Test #15
C ₄ -Benzene	0.05	0.05
C ₄ -Benzene	0.10	ND
C ₅ -Cyclohexane	ND	0.05
n-C ₁₁	0.60	0.80
Alkane	0.05	0.10
C ₄ -Benzene	0.05	0.05
C ₅ -Cyclohexane	0.10	0.15
Alkane	0.10	0.15
Alkane	0.10	0.15
C ₅ -Benzene	0.35	0.35
C ₅ -Benzene	0.10	0.10
Tetrahydronaphthalene	0.10	0.10
Naphthalene	0.25	0.05
n-C ₁₂	1.00	1.00
C ₆ -Benzene	0.15	0.15
C ₆ -Cyclohexane	0.35	0.35
C ₆ -Benzene	0.15	0.15
C ₁₄ H ₃₀ (branched alkane)	0.30	0.35
C ₆ -Benzene	0.05	0.05
Methyl Tetrahydronaphthalene	0.10	0.10
n-C ₁₃	0.95	1.00
C ₁₄ H ₃₀	0.10	0.10
2-Methyl Naphthalene	0.20	0.05
C ₇ -Cyclohexane	0.15	0.15
C ₁₄ H ₃₀ (branched alkane)	0.05	0.05
C ₁₅ H ₃₂ (branched alkane)	0.25	0.25
C ₂ -Tetrahydronaphthalene	0.05	0.05
n-C ₁₄	0.70	0.75
C ₁₅ H ₃₂ (branched alkane)	0.10	0.10

TABLE 27. GC/MS IDENTIFICATION OF EXHAUST AND FUEL COMPONENTS (Concluded)

Component (a)	Relative Concentration (n-C ₁₂ = 1.00)	
	XAD Test #15	Fuel Test #15
Dimethyl Naphthalene Isomer	0.10	<0.01
Dimethyl Naphthalene Isomer	0.10	<0.01
C ₁₆ H ₃₄ (branched alkane)	0.35	0.35
n-C ₁₅	0.40	0.40
n-C ₁₆	0.20	0.20
C ₁₆ H ₃₄ (branched alkane)	0.05	0.05
n-C ₁₇	0.05	0.05

(a) Compounds listed in order of retention time.

TABLE 28. SELECTED AROMATIC/ALIPHATIC HYDROCARBON RATIOS
FOR EXHAUST AND JP-5 FUEL

Components	Concentration Ratio	
	Exhaust (Test 3)	JP-5 Fuel (Test 3)
C ₄ -Benzenes/n-C ₁₁	0.44	0.26
Naphthalene/n-C ₁₂	0.38	0.11
1-Methyl Naphthalene/n-C ₁₃	0.15	0.0099
Dimethyl Naphthalenes/n-C ₁₄	0.33	0.058
Phenanthrene/n-C ₁₆	0.17	0.012

phenomenon appears to represent selective survival of the aromatics during the combustion process, since formation of alkylnaphthalenes by radical coupling processes is highly unlikely.

The data for PNAs obtained by GC/MS (MID) are presented in Table 23. These data reveal appreciable quantities of PNAs in the distillation range of the fuel (i.e., naphthalene, alkylnaphthalene, and phenanthrene/anthracene). Significant quantities of higher-molecular weight PNAs (fluoranthene to benzo(a)pyrene) were detected. No PNAs having molecular weights greater than benzo(a)pyrene were detected. No polar-substituted or heterocyclic PNAs were detected. However, highly specialized techniques such as negative ion chemical ionization GC/MS were not employed to search for polar PNAs (e.g., nitro PNAs).

3. Carbon Balance

One of the more important aspects of this project is the accountability of organic species in turbine engine exhaust. Previous studies have accounted for only a fraction of the total organic emissions. Assessment of the toxicity and photochemical smog reactivity of such emissions requires a more detailed knowledge of organic distribution than past studies have provided.

The normal method of ascertaining the degree to which some component in an exhaust stream is accounted for is to attempt a mass balance. In the case of organics, the mass balance is based on carbon and is termed a "carbon balance." Ideally, carbon balance is defined as the ratio of the sum of all individual organics measured in the exhaust, divided by the total organic concentration. As discussed in Section II E, two techniques can be used to determine the total organic concentration. One, known as EPA Method 25, is designed to respond equally to all organic carbon atoms. The other method, Flame Ionization Detection (FID), responds nearly equally to all carbon atoms bound to carbon or hydrogen, but is nearly insensitive to oxygenated carbon atoms. Comparison of the sum of species with Method 25 total organics is straightforward, since each carbon is counted as 1.0. However, to compare the species sum with total FID response in a fair manner, the species sum must be adjusted to eliminate contributions from oxygenated carbon. As discussed in Task 1, this means formaldehyde is not counted in the species summation; only one of the acetaldehyde carbons is counted; etc.

During the Task 2 combustor rig studies, both Method 25 and FID were employed to determine "total organics" in the exhaust. Unfortunately, the subcontractor performing the Method 25 analyses was unable to report results for the first eight runs due to contamination of the samples in their laboratory during analysis. Of even greater concern, the Method 25 results for the six combustor rig tests for which data were obtained are highly scattered and inconsistent. These data are shown in Table 17. Two independent FID instruments showed the level of organic emissions to be reasonably constant throughout these six runs, but the Method 25 results show dramatic run-to-run variations. In addition, the Method 25 values should always equal or exceed the corresponding FID data, but for five of the six runs Method 25 was less than the FID value. Indeed, for four of the six experiments it was less than the species sum. The scattered and inconsistent Method 25 results preclude the use of these test results in calculating a carbon balance.

Two independent FID measurements are available for the combustor rig experiments. These results are shown in Tables 11 and 24, respectively. The Battelle FID results (Table 24) are slightly but consistently higher than the GE data (Table 11). This difference is caused by the different rake positions sampled by the two instruments. The results from the Battelle monitor are used in determining carbon balance because the instruments used to determine organic species obtained their samples from the same rake position.

The carbon balances for the 12 combustor rig exhaust experiments are presented in Table 29. The carbon balances range from 80 to 95 percent. On the average, 88 percent of the organic emissions from the combustor rig were accounted for as individual constituents by the sampling and analytical methods. An average 88-percent carbon balance is a major improvement over the accountability obtained in previous aircraft engine experiments.

4. Method Performance Characteristics

a. Cryogenic Sampling

The precision obtained for the cryogenic sampling was excellent (~5- 10 percent), in most cases, as shown in Tables 13-16. This level of precision was obtained for a wide variety of compound classes,

TABLE 29. COMPARISON OF ORGANIC SPECIES SUM WITH TOTAL FID
RESPONSE FOR COMBUSTOR RIG EXHAUST

Run No.	Total Organics by FID, ppmC	Total Organics by Species Summation, ppmC*	Carbon Balance, %
2	600	534	89
3	585	528	90
4	580	520	90
6	600	552	92
7	595	475	80
8	570	520	91
10	515	447	87
11	510	423	83
12	500	421	84
14	525	472	90
15	495	472	95
16	490	436	89
Average			88

* Corrected for oxygenated carbon response.

including aliphatics, aromatics, olefins, aldehydes, and ketones. Although the absolute accuracy of the technique cannot be determined with certainty from these data, the good carbon balance obtained, coupled with the fact that over 60 percent of the total hydrocarbons were in the cryogenic sampling region, attests to the accuracy of the technique (as do the Task 1 data).

b. XAD Sampling

The XAD sampling and analysis procedure gave good precision (5 to 10 percent) over the $n\text{-C}_9$ to $n\text{-C}_{17}$ volatility region. Good agreement was obtained between the XAD and cryogenic sample data for $n\text{-C}_9$ and $n\text{-C}_{10}$, for which both techniques can be used. However, the cryogenic sampling data for $n\text{-C}_{11}$ and naphthalene were 20 to 25 percent greater than the XAD data. This result appears to be from the baseline rise caused by the unresolved envelope discussed earlier. The XAD analysis technique employs a data system which can compensate for this rise whereas the cryogenic system does not, hence causing artificially elevated values for these late eluting peaks. Consequently, the XAD data for these compounds ($n\text{-C}_{10}$ and greater) are considered to be more accurate and have been used in all of our carbon balance calculations, etc. Backup traps (in series with primary traps) and background air samples contained no significant quantities of organics.

c. PNA Analysis

PNA analysis data have been presented in Table 22. Acceptable agreement was obtained between the three test samples analyzed (Tests 3, 11, and 14), although Test 3 gave elevated levels of most of the components, compared to Tests 11 and 14. Very low levels of PNAs were observed in the background air samples and backup traps, indicating good blank levels and collection efficiencies for the PNAs. Recoveries of 80 to 130 percent were obtained for the two traps (Tests 10 and 15) spiked with selected PNAs prior to sampling.

d. Aldehyde Analysis

Data for aldehyde analysis are presented in Table 21. Low quantities of aldehydes (<20 percent of the primary impinger) were found in the backup impingers, as well as the background air samples, indicating good collection efficiency and freedom from contamination. Excluding Tests 2 and 15, reasonable precision (± 10 to 20 percent) was obtained for formaldehyde, acetaldehyde, acrolein, and propional. Less precise results were obtained for crotonal and benzaldehyde, probably due to the lower concentration of the compounds.

Because of the high level of formaldehyde (~ 12 ppm), the sample was diluted tenfold prior to analysis. In future work we plan to analyze the extracts undiluted, as well, to improve the precision for the less abundant aldehydes. The reasons for the wide discrepancy between Tests 2 and 15 and the remaining tests is not known, although the sample line was changed just prior to Test 15, and this may have been a contributing factor. Since benzaldehyde is readily analyzed by the cryogenic sampling technique, that technique will be used for quantification in Task 3.

Agreement between the acetaldehyde value by the DNPH technique (~ 5 ppmC) and cryogenic sampling (3 to 5 ppmC), as well as acrolein (6 versus 8 ppmC), is acceptable, considering the reduced GC/FID response factor (0.6 to 0.7) for these compounds and the 60-percent DNPH recovery factor for acrolein determined in Task 1.

Although the aldehyde data are not as reproducible as the XAD and cryogenic hydrocarbon data, this result does not seriously affect the usefulness of the results since (1) reasonable precision is obtained for the major aldehydes and (2) these compounds, while important photo-chemically, are not a major portion of the hydrocarbon emissions.

e. Alcohols

During the current program, methanol and ethanol analyses of the combustor rig exhaust have been accomplished by direct injection (0.25 ml) onto a gas chromatograph coupled to a photo-ionization detector. Figure 13 shows a chromatogram from an actual sample along with the expected

elution of methanol and ethanol. Figure 14 depicts the chromatogram from the same sample after spiking the contents with 10 ppm ethanol. One can see from these chromatograms that methanol is sufficiently resolved from the exhaust components while ethanol is only partially separated. Based upon compound response factors, it is clear that methanol and ethanol concentrations in the combustor exhaust are each below 1 ppm.

Although the above experiments proved successful, repeated runs could not duplicate the same results. In the subsequent runs the spiking experiment did not result in a partially resolved ethanol peak but rather co-eluting peaks. Attempts to improve chromatographic conditions were restricted by limitations in the oven and flow design of the GC instrument.

D. CONCLUSIONS

The results obtained in Task 2 are encouraging in that (1) good carbon balance (88 percent) was obtained by comparing the total hydrocarbon concentration by FID to the summation of hydrocarbon species determined by the various sampling and analysis techniques, (2) a major portion (~60 percent) of the total hydrocarbon content was attributed to specific compounds on the basis of GC/MS identification techniques, and (3) the various sampling and analysis systems work very well in terms of precision, collection efficiency (determined from backup traps) and agreement between methods for the compounds overlapping the various methods.

Although certain improvements in the methods could be helpful, the existing sampling and analysis systems are considered adequate for completion of Tasks 3 and 4.

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